DTIC
S ELECTE
JUL 15 1993
A D

AD

PREPARATION AND INVESTIGATION OF IMPROVED LOW VOLTAGE ELECTRON EXCITABLE PHOSPHORS

Annual Technical Report

by

S S Chadha, D W Smith and A Vecht
May 1993

United States Army

EUROPEAN RESEARCH OFFICE OF THE US ARMY

London   England

CONTRACT NUMBER DAJA-45-92-C-0007

University of Greenwich

Approved for Public Release; distribution unlimited

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 1993	Annual Report May 92-May 93

4. TITLE AND SUBTITLE

Preparation and Investigation of Improved Low Voltage Electron Excitable Phosphors

5. FUNDING NUMBERS

6. AUTHOR(S)

S S Chadha, D W Smith and A Vecht

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

DAJA45-92-C-0007

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Recent advances in the area of field emitting arrays point to the possibility of fabricating low voltage variants of the CRT. However, these advances also highlight the lack of suitable low voltage excitable phosphors. The aim of this contract is to remedy this situation and to provide suitable phosphors emitting RGB. The problem is being tackled by making either intrinsically or extrinsically conducting phosphors, the latter by the addition of suitably conducting fine particle powders. In addition, the evaluation of phosphors has been possible by acquiring a low voltage demountable CRT system. Thus far, the results from our experiments have been promising. A bright, pure green emitting phosphor ($ZnGa_2O_4:Mn$) and a novel red emitting phosphor ($CaTiO_3:Pr$) have been made. In-house prepared bluish-green emitting ZnO:Zn has been shown to be as bright as the commercial ZnO:Zn phosphor. Photoluminescent thin film variants of both ZnO:Zn and $ZnGa_2O_4:Mn$ have been made using aerosol spray pyrolysis techniques.

Therefore, we now have three low voltage phosphors instead of only one available at the start of this contract. Our aims are to optimise these phosphors further and to attempt other lattices. Small sealed devices will be made to simulate conditions in real FED devices and phosphors will be supplied to any US FED manufacturer.

Keywords: Phosphors, low voltage, field emission devices, ZnO:Zn, $ZnGa_2O_4:Mn$, $CaTiO_3:Pr$, $SnO_2:Eu$, $Zn_2SnO_4:Eu$, thin films, MOCVD, aerosol spray pyrolysis.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

ABSTRACT

This report covers the work carried out in the first year of the contract to investigate new and improved low voltage phosphors for field emission displays (FEDs). The work commenced with a literature survey of relevant papers and patents and attempts to determine suppliers of phosphors, with particular reference to suitable low voltage materials. Not surprisingly, very few manufacturers of low voltage phosphors were unearthed and these only supplied ZnO:Zn. Hence, at the commencement of this contract, only one low voltage phosphor was available.

Our work during this period has concentrated on assessing new lattices, attempting to obtain high surface conductivities from nominally insulating materials, as well as setting up a low voltage, demountable cathodoluminescent rig. In addition, our research efforts have been geared towards ensuring that we were not dependent on external suppliers for ZnO:Zn phosphors. Hence, this aspect also received considerable attention.

Three interim reports have been issued, together with samples of many types of phosphors prepared in our laboratories. Some of these have been evaluated by our colleagues at Fort Monmouth and the results so far have been very promising. As a result of our efforts, a phosphor system emitting saturated green ($ZnGa_2O_4$:Mn) and another emitting orange-red ($CaTiO_3$:Pr) have been successfully produced.

The luminance levels measured at Fort Monmouth EDTL, were:

ZnO:Zn	˜{2600 ftL (UG)
	˜{2700 ftL (commercial)
$ZnGa_2O_4$:Mn	350 ftL
$CaTiO_3$:Pr	160 ftL

Hence, within our first year, we have produced a phosphor system emitting a bluish-green (ZnO:Zn), green ($ZnGa_2O_4$:Mn), and an orange-red ($CaTiO_3$:Pr), all with a low threshold voltage. Obviously, for a RGB system, the colour purity will not be perfect and filters will be required at this stage especially to obtain a blue from the ZnO:Zn phosphor.

DTIC QUALITY INSPECTED 8

2

INTRODUCTION

In the past year, the work on this contract has been carried out in the following areas:

1) Literature Search

A literature search was carried out at the beginning of the contract. Most patents were of Japanese origin. Only a few patents covering phosphor preparation techniques were uncovered. The complete list of references was given in the first interim report. Since then, only a few papers and patents have been found in the literature. These have been listed in the other interim reports.

2) Phosphor Suppliers

A list of phosphor suppliers was appended in the first interim report. All these suppliers were approached for information on any phosphors for low voltage application. Only Kasei, PTL (UK) and Hoechst responded but only Kasei appeared useful.

3) ZnO:Zn Powder Phosphor

Introduction

We decided upon two routes for our investigations into producing luminescent ZnO powder phosphors. The first route employed nominally high purity, commercially available ZnO powder with the appropriate particle size. The suppliers included Koch-light, Merck Ltd., Rose Chemicals, Grillo Zinc Oxide and Koch Chemicals. The second route involved the preparation of ZnO from various high purity raw materials such as carbonates, sulphates and nitrates.

a) Preparation of ZnO:Zn from ZnO powders

High purity ZnO powder was obtained from various com-mercial suppliers. After studying the effects of milling, sieving, batch size, atmosphere, firing time etc., a set of optimum conditions was arrived at. These are listed in Table 1. The average size of the ZnO:Zn powder particles was around $1-2\mu m$.

Table 1. Optimum conditions for the Preparation of ZnO:Zn Phosphor

Process	Conditions
Sieving	Yes
Prefiring temp.	600°C
Prefiring time	30 mins.
Resieving	Yes
Firing time	60 mins.
Firing temp.	1000°C
Atmospheric conditions	Reducing

As a result of this optimisation, the batch size was increased from 2-3g to 40g. Though most batches produced good phosphors, there have been instances where caking and/or over reduction occurred. Mostly this is due to uneven exposure of the ZnO material to the reducing atmosphere. Hence, a rotary furnace has been purchased to ensure even surface exposure.

b)   Preparation of ZnO from various Zn salts

As noted earlier, the second route for the manufacture of ZnO:Zn involves the preparation of a zinc salt which can be thermally decomposed to produce ZnO.

This route should have the advantage that the purity, and possibly the particle size of the starting material, can be controlled. Initial studies were carried out using zinc sulphates, nitrates and acetates. These were converted to either the oxalate or the carbonate. High purity was ensured using cross precipitation techniques. The carbonates and oxalates were heated to form ZnO at around 600-700°C. The ZnO:Zn phosphor was formed by reducing the ZnO at 1000°C.

The carbonates normally led to greyish ZnO and the oxalates to a white material. It was found that phosphor prepared from the sulphate via the oxalate route was the best. Addition of some elemental S to the ZnO prepared from Zn acetate via the oxalate route also led to bright ZnO phosphor. It thus appears that the presence of a minute quantity of S, either deliberately added or present as a result of using the $ZnSO_4$, seems to be beneficial to the PL. However, from the literature   , S is not a preferred species in ZnO phosphors, since the electron gun source can be poisoned.

c)   ZnO:Zn phosphor assessment

The assessment of the ZnO:Zn phosphors was carried out using material examination techniques such as XRD, SEM, ICP, as well as PL studies using both laser and UV excitation and CL studies using both low and high voltage sources. For reference, the best commercially available ZnO:Zn was used.

c.i) XRD

XRD examination of ZnO (raw), ZnO with added S and ZnO prepared from $ZnSO_4$ via the Zn oxalate route, revealed no discernible differences (Figs. 1-3).

c.ii)   SEM

SEM examination of ZnO revealed that the particle size was around 1-2μm. The commercial material was similar, (Figs. 4 and 5) both in size and in morphology.

c.iii) ICP

Chemical analysis to determine the impurity level in some of
the phosphors prepared from commercial ZnO samples, ZnO:Zn
prepared via the chemical methods, as well as commercial
ZnO:Zn, was carried out using inductively coupled plasma
spectroscopy. The results of this exercise are tabulated
below:

	Elements (ppm)						
Phosphor sample	Cd	Ni	Ca	Cu	Fe	Pb	Mn
Commercial ZnO:Zn	0.965	0.760	0.082	0.028	0.138	1.67	0.054
BDH-ZnO	0.944	0.752	0.102	0.074	0.012	5.11	0.052
Rose Chemical-ZnO	1.4	0.761	0.074	0.039	0.074	5.66	0.053
$ZnSO_4$-Zn oxalate-ZnO	0.906	1.19	0.433	0.203	0.326	4.18	0.065
$ZnAc_2$-Zn oxalate-ZnO $ZnAc_2$	0.932	0.751	0.496	0.171	0.153	4.35	0.074

As can be seen, most impurities levels are very similar.
The major differences are in the levels of Ca, Cu and, in
one instance, Fe. Hence, overall, it is difficult to judge
why some materials yield a good phosphor, whilst another
yields a poor phosphor. The major problem with ZnO is that,
unlike other phosphors which require activators and/or co-
activators, it is self-activated. This imposes very severe
restrictions on the preparation conditions. The Zn-O
dissociation plot is shown in Fig. 6.

c.iv)   Photoluminescence

Over the year, the PL, under laser excitation, of ZnO:Zn
phosphors prepared in-house, has approached, but more often
exceeded, that of the commercial material. Under UV
excitation, ZnO:Zn emitted as intense whitish-green
luminescence. The excitation and emission spectra are shown
in Fig. 7. The broad emission peak of the ZnO:Zn is centred
around 505nm (FWHM 120nm). The decay time t was very short,
~0.3μs (where t is defined as the time for the initial PL

intensity to decrease by a factor $1/e$ (Fig. 8).

c.v)   Cathodoluminescence studies

CL studies have been mainly carried out at ETDL, Fort
Monmouth, though some preliminary evaluations were done at
the University of Greenwich using the set up shown in Fig.
9. The phosphor layers for evaluation were prepared by
either doctor blading or electrophoresis. Typical B-V and
luminance-time results are shown in Figs. 10 and 11. The
main reason for the apparently poor stability is probably
adsorbed moisture and oxygen. In the initial tests when no
baking was used, the stability was very poor. After removal
from the vacuum test chamber, a heavy browning (burning?)
was observed at the point where the e-beam impinged on the
phosphor.

When the layers were baked using a quartz lamp projector focused onto the sample, the stability was improved dramatically. The browning was reduced considerably. It is hoped to repeat these tests in the near future with better control and monitoring of the baking conditions.

At Fort Monmouth, the results obtained were as follows:

Phosphor	Luminance at 1500V (ftL)
ZnO:Zn (Greenwich)	2600
ZnO:Zn (commercial)	2700

Hence, the ZnO:Zn is as good as the commercial material.

Though this contract is for low voltage ZnO:Zn, CRTs made using phosphors prepared in-house and commercial phosphor have given rather promising results at 15 keV.

Phosphor	Efficiency (lm/W) at 15kV	
	$1\mu A/cm^2$	$8\mu A/cm^2$
ZnO:Zn (Greenwich)	4.9	4.2
ZnO:Zn (commercial)	2.1	1.25

4) ZnGa$_2$O$_4$:Mn Powder Phosphor

a) Preparation

We have had considerable success with the synthesis of
ZnGa$_2$O$_4$:Mn phosphors. The initial samples were synthesised
by the solid state reaction of the specific oxides at
elevated temperatures. The mixtures were prefired at lower
temperatures in order to properly dehydrate the oxides and
to provide a more homogeneous mixture. The final firing was
always in an atmosphere such that the manganese was reduced
to the Mn^{II} state. The reduction of the manganese to the $^{+2}$
state was accomplished by firing in an atmosphere of carbon
monoxide. As judged by the eye, this led to a phosphor with
a long PL persistence. Covering the phosphor layer surface
with a layer of powdered charcoal during firing led to a
significantly reduced persistence.

ZnGa$_2$O$_4$:Mn has been prepared with up to 1% Mn. A range of
temperatures up to 1300°C has been used, though, in order to
restrict the particle growth no fluxes have been added.
The higher temperature gave more consistent results.
Attempts to substitute Ga with Al led to poor phosphor so
this route of investigation was not pursued.

b) ZnGa$_2$O$_4$:Mn assessment

The assessment of the ZnGa$_2$O$_4$:Mn was carried out using XRD
and SEM (Fig. 12), as well as PL and CL measurements, using
both low and high voltage sources.

b(i) CL and PL analysis

The ZnGa$_2$O$_4$:Mn emits a purer green luminescence than ZnO:Zn.
The excitation and emission spectra are shown in Fig. 13.
The narrow band emission peak is centred around 505nm with a
decay time ($^1/_e$) of around 4 mS. (Fig 14). Some phosphor
exhibited a short persistence whilst others appeared to show
a longer persistence when judged by eye, (see XRD section).
A typical emission spectrum under CL excitation is shown in
Fig. 15.

Investigation at 15keV gave the following results:

Phosphor	Efficiency (lm/W) at 15keV	
	1μA/cm^2	8μA/Cm^2
ZnGa$_2$O$_4$:Mn	4.7	4.4

Unfortunately, no commercial ZnGa$_2$O$_4$:Mn is available, but
the PL under 254nm compared well with commercial MgGa$_2$O$_4$Mn.

Electrophoretically deposited layers of $ZnGa_2O_4$:Mn were measured at ETDL and a B-V curve is shown in Fig. 16. More importantly, the stability of the gallate was extremely promising as shown in Fig. 17.

b(ii)   **XRD**

XRD spectra have been obtained for both the long and short persistence material. However, no structural differences were found (Figs 18 and 19).

5)   Calcium Titanate:Pr (CAT)

This phosphor is not available commercially. A pinkish-red emission with a substantial afterglow is obtained when excited by either long (366nm) or short (254nm) wavelength UV.

The emission of the system was optimised for firing temperature and time, Ca:Ti ratio and activator concentration. A total of three hours firing in four stages at 1000°C and 1100°C was necessary, the last firing being in a slightly reducing atmosphere. The best results were found with relatively low (<0.2 at. %) concentrations of praseodymium in a matrix with stoichiometric (1:1) proportions of calcium to titanium. Praseodymium was replaced by 12 other rare earths at 0.1 at. % and 0.5 at. % concentrations in the optimised formulation but the PL of the Pr activated phosphor was at least an order of magnitude more intense than any of the others. Potassium carbonate flux, excess of which was subsequently washed out, considerably enhanced the emission.

Other group II elements, both IIA and IIB, were partially substituted for calcium, with mostly detrimental effects on the photoluminescence. The emission colour was unchanged. However, substitution of up to 50% of the calcium by strontium gave a brighter phosphor under UV with a much shorter afterglow. This is summarized in Table 2.

TABLE 2

Subjective Evaluation of Calcium Strontium Titanates:Pr

	Ca:Sr 1:0	Ca:Sr 3:1	Ca:Sr 2:1	Ca:Sr 1:1	Ca:Sr 1:3
*Photoluminescence (254nm excitation)	7	8	9	10	3
*Photoluminescence (366nm excitation)	5	9	10	10	3
Persistence	long	long	long	short	v.short

*The numbers are subjective estimates of the PL intensity on a scale 0 (weakest) to 10 (strongest).

The XRD spectrum of $CaTiO_3$:Pr is shown in Fig. 20. From the SEM micrograph (Fig. 21), it appears that the particles consist of agglomerates of about 5μm composed of fine hexagonal crystals of 1μm and less.

Although the phosphor was initially developed for excitation by UV, the emission under CR bombardment was found to be

substantial. The emission spectra derived from both laser
and cathode ray excitation are shown in Figs. 22 and 23, the
peaks coinciding at 615nm. Interestingly, under high or low
loading, the variation of cathodoluminescent intensity does
not appear to follow the pattern for photoluminescence noted
above when calcium is partially replaced by strontium. This
is illustrated in Fig. 24 (high loading). The CL comparison
will only be valid if the coatings are identical (thickness,
particle distribution). The brightness-voltage curve for
$CaTiO_3$:Pr at low loading is shown in Fig. 25.

Although the luminance output of the phosphor drops with
time (Fig. 26), this is matched by a corresponding current
drop, indicating that the efficiency remains substantially
unchanged.

To improve its performance at low voltages, a number of
mixtures of the phosphor with conducting ITCO powder have
been prepared. Other samples of the phosphor have been
coated with ITCO all attempting to improve the low voltage
performance (see sections 10 and 11). These formed part of
the deliverables for the fourth quarter.

6) SnO$_2$:Eu

Pure SnO$_2$ powder from Aldrich was used for the preparation of SnO$_2$:Eu phosphors. The Eu was added as the chloride after conversion from the acetate. Firings were carried out with and without fluxes. Fluxes used included NaCl, BaCl$_2$, NH$_4$F, NH$_4$Cl and mixtures thereof. Firings were carried out in the range 1200 to 1600°C. Firing times varied from 1-2 hours for the first firing and 1-2 hours for the second firing. The Eu concentration was varied from 0% to 10%.

Fluxes

Best results were obtained using NaCl and BaCl$_2$ fluxes. When the flux concentration was low, the resulting sample was a soft, crusty cake, whereas 40% flux led to a very hard cake. Phosphors with no flux produced very little luminescence. The highest PL was observed from phosphors with 20% flux. Phosphor samples made with different fluxes form part of the deliverables for this quarter.

Firing temperature

A trend was noted in the PL intensity as a function of the firing temperature, with PL intensity increasing steadily between the range 1200-1600°C. However, as the furnace was only rated for 1600°C maximum, most phosphors were fired at 1550°C to extend the life of the open elements. A second firing did not lead to any improvement in the PL intensity.

Firing time

Samples fired for one hour were fairly soft but those fired for two hours became crusty. This is probably because of particle size growth and maybe sintering. In general, samples fired for longer times were brighter.

Dopant concentration

No PL was observed from undoped SnO$_2$ after firing, and samples with 0.1 and 0.5% Eu dopant emitted a bright orange/red colour. The PL intensity decreased as the Eu con-centration was increased from 1% to 10%.

SEM and XRD Analysis

A SEM micrograph of the SnO$_2$:Eu phosphor is shown in Fig. 27 and the XRD analysis in Fig. 28. A large variation in particle size was observed. XRD spectrum matched commercial SnO$_2$ powder.

7)   Zinc and Cadmium Stannates

This possible phosphor system may have certain advantages, if Eu activation is possible, over the SnO_2:Eu system. In particular, Cd_2SnO_4 is a known conductor, if efficient luminescence could be obtained, it should be suited to excitation by low voltage cathode rays.

The synthesis of Zn_2SnO_4:Eu was carried out via a standard phosphor route by firing the mixed oxides of zinc and tin at temperatures up to 1500^oC for periods from half-an-hour to three hours in an oxidizing (air) atmosphere. A range of Eu from 0% to 5% was added, as well as a flux consisting of equal parts of sodium and barium chlorides, up to 20% by weight. The fired powder was washed free of flux.

The best activated phosphor contained 2 at. % Eu but showed only very weak orange-yellow PL under 366nm UV and an even weaker pink emission under 254nm. Substitution of all or part of the zinc by cadmium gave powders with intense body colours which were not luminescent. The zinc compounds were insulating while the cadmium compounds were, not un-expectedly, conducting.

The brightest phosphor contained no added europium, giving a whitish emission under 254nm and a stronger greenish-yellow under 366nm. The intensity, although still rather weak, was estimated to be at least an order of magnitude greater than from Zn_2SnO_4:Eu.

The particle size and morphology of both unactivated and Eu activated phosphor were similar when studied under the SEM. Unactivated Zn_2SnO_4 is shown in the microphotograph in Fig. 29. The XRD spectra of the two types were also similar (Fig. 30), showing evidence of unreacted ZnO and SnO_2 in the phosphors. This was still true even after firing for 16 hours.

So far, this system has shown little promise, but samples of both Eu activated and unactivated Zn_2SnO_4 were submitted as part of the 4th quarter deliverables in case the behaviour of this phosphor under CR excitation was substantially different to that under UV.

8)   Zinc Oxide:Zn Thin Films

Over the last six months, significant progress has been made in producing luminescent ZnO:Zn thin films.

The method employed is aerosol spray pyrolysis (ASP) in which a fine mist of an organo-zinc compound, dissolved in an organic solvent, is passed over a suitable substrate which is heated to a temperature between 430°C and 470°C. The zinc compound is pyrolysed to ZnO at the hot substrate surface.

A sketch of the apparatus is shown in Figs. 31 and 32. The solution of zinc acetylacetonate in acetone/ methoxyethanol is delivered to the nebulizer at the top of the three-necked flask (Fig. 31). The nebulizer gas can be either nitrogen or air. A second gas inlet to the flask enables the ratio of $N_2:O_2$ in the mist carrier gas to be altered. The mist is delivered to the reaction chamber (Fig. 32a), comprising a rectangular section tube, into which the platform bearing the substrate is inserted (Fig. 32b). A tube of rectangular section is preferred to a circular tube because this yields a laminar rather than turbulent gas flow over the substrate.

Initially, borosilicate glass (Corning 7059) substrates were used. No photoluminescence was detected in the films as deposited. Films were then annealed at elevated temperatures in both oxidizing (air) and reducing (carbon monoxide) atmospheres. No photoluminescence could be detected at temperatures below the softening point of the glass. Above the softening temperature there was a very weak orange photoluminescence.

Subsequently, sapphire discs have been used as substrates, enabling higher annealing temperatures to be used. Consequently, the PL was somewhat stronger. Films less than $0.6\mu m$ thick were transparent with an orange PL, stronger when viewed in the reflective mode from the reverse side. In thicker films ($0.9-1.1\mu m$), the PL was green after annealing in air, becoming bluer on annealing in a reducing atmosphere. These films were opaque after firing. The thickness of the films can be rapidly estimated from a UV/Vis spectrum by applying the formula

$$t = \frac{\lambda_2 \lambda_1}{2n (\lambda_2 - \lambda_1)}$$

where λ_2, λ_1 are the wavelengths of successive nodes and n is the refractive index of ZnO (taken as 2). The method fails, of course, for films where considerable scattering occurs. A typical spectrum is shown in Fig. 33. An SEM of unannealed ZnO grown on glass is shown in Fig. 34.

The film growth rate of 10 nm/min. is undesirably slow, possibly due to the rapid carrier gas flow rate causing undue cooling at the substrate surface. The high carrier gas rate is necessary for the efficient functioning of the nebulizer. The reaction tube is therefore undergoing modification to reduce the flow rate. Increased growth rates can also be induced by using more concentrated solutions although this can create problems by blocking the nebulizer.

Apart from depositing ZnO thin films by ASP, other techniques for synthesis of ZnO thin films are being investigated. Photoluminescent samples prepared by ASP, and one sample prepared by another method, have been submitted for evaluation.

9)   Zinc Gallate:Mn Thin Films

Early results from attempts to make $ZnGa_2O_4$:Mn thin films were very promising. The apparatus used and the procedures followed were almost identical to that previously described for ZnO:Zn films (Section 8) i.e. aerosol spray pyrolysis followed by high temperature annealing.

The solution used for the gallate was a mixture of the acetylacetonates of zinc, gallium and Mn^{II} in a molar ratio of 1:1:0.01 respectively in a mixed acetone/metho-oxyethanol solvent. The sapphire substrates were held at temperatures of 430-470°C.

The as-deposited films were pale brown and not photo-luminescent. Because of their opacity, an estimate of the thickness of the films could not be obtained from a simple UV/Vis spectrum (Fig. 35). However, this did demonstrate that the band edge had been shifted to 275 nm compared with 371 nm for ZnO, indicating the probable formation of zinc gallate at the substrate surface before annealing.

Photoluminescence was induced in the films by annealing at 1000°C for short periods of up to 20 minutes, mainly in reducing atmospheres. The PL was/far more intense than that found in the ZnO:Zn films and of a colour that was, to the eye, typical of $ZnGa_2O_4$:Mn powder phosphor. The XRD spectrum of the film was also identical to that of the powder with respect to the 2θ values of all the peaks although obviously, the peak intensities differed (Fig. 36 cf, Figs. 18 and 19).

The SEM micrographs of gallate films or glass substrates adjacent to the sapphire substrate in the reaction chamber indicated that the film thickness was about 1-2.5μm with a steep thickness gradient from the front to the back of the reaction chamber. It was found that the thicker the film, the more intense the PL. These films are about twice as thick as the ZnO:Zn films with a growth rate at least twice as fast.

The process for depositing $ZnGa_2O_4$:Mn films has by no means been optimized. Further work is necessary with the precursor solutions, growth conditions and, more particularly, the annealing temperature atmosphere and uniformity of film thickness.

10) Conducting ITCO Powder

For use in low voltage devices, cathode ray phosphors must either be intrinsically conducting, as in ZnO:Zn, or may be made so by forming a conducting layer on the particles. Alternatively, the phosphors may be mixed with a conducting powder. We are investigating both methods. As noted in previous interim reports, conducting indium oxide powder has been synthesized. Pure In_2O_3 (99.99%) was doped with tin chloride and cadmium chloride. After firing at $850^{\circ}C$ and milling, the pale yellow powder exhibited a bulk conductivity of ~400 ohms (cf. ZnO:Zn->20M ohms). The size of the ITCO particles was around 100 nm.

A graph showing the change in resistance as a function of varying the Sn concentration in ITCO powder is shown in Fig. 37. As can be seen, there is a minimum resistance at concentrations of ~6% in the ITCO powders. Firing in a reducing atmosphere leads to a doubling of conductivity of the ITCO powder.

Early attempts to make layers of $InBO_3$:Tb phosphor with ITCO powder for use in the CL system led to indifferent results. The body colour became darker. However, the addition of a small quantity of TiO_2 led to improved results. The change in the threshold voltage, Vth, is shown in Table 3, where Vth refers to the point at which visible luminescence appears. Such conducting powders will be useful where attempts to synthesise conducting coatings fail. Some coating experiments are described in the next section.

TABLE 3

% In_2O_3	Vth
0	>1500
5	1500
10	1000
20	600

11) Coating of Conducting Materials on InBO$_3$:Tb and CaTiO$_3$:Pr (CAT) Phosphors

For the preparation of conductive layers, In acetylacetonate (In(acac)$_3$) and dibutyl tin diacetate (DBTA) were used in various ratios and solvents. The results of coating InBO$_3$ powder phosphor particles with In$_2$O$_3$ appeared promising. The surface became conductive and the PL intensity decreased, indicating possible absorption of the UV by the ITCO film/layer. However, SEM analysis revealed no differences between the coated and the uncoated material.

Coating experiments were also attempted on our novel red phosphor (CaTiO$_3$:Pr). The bulk resistance of the CAT was 12M ohms. The results of coating with ITCO using varying amounts of Sn are given in Table 4.

TABLE 4

% Concn. Sn in In$_2$O$_3$	Resistance	Resistance after firing in reducing atmosphere
Control	12 M ohms	
0	180 k ohms	
0.22	130 "	
0.43	21 "	650 ohms
0.87	15 "	
1.72	6 "	
4.19	2 "	
8.06	12 "	400 ohms
11.22	50 "	
14.91	25 "	

12) Low Voltage Demountable Cathodoluminescent Apparatus

A low voltage (50eV-1500eV range) system, centred around a Kimball Physics EFG-7 Flood Electron Gun, has been set up. The vacuum system employs a turbomolecular pump. The circular chamber has six ports on the side and one on top. Photographs of the system are shown in Figs. 38 and 39. Significant delays occurred in obtaining both the gun system and the vacuum chamber. However, the system has now been installed and is ready to run. A suitable spectrometer is being sought and we have had demonstrations from various suppliers.

13) Commercial Phosphors

At the beginning of this contract, a letter was sent to various phosphor suppliers, seeking prices and delivery dates. Only Kasei Optonix responded (Section 2). In turn, we have supplied phosphors to MCC. According to them, over 8000 ftL were achieved using our $ZnO:Zn$ phosphor. Over the past year, we have made contact with many US companies who are actively engaged in FED research.

14) Conclusions

In the first year of the ARPA contract no. DAJA-45-92-C-0007, considerable, verifiable progress has been made in achieving the main objectives of this proposal outlined at the beginning of this report and summarised below.

As is well known, at the start of this proposal, only one phosphor, namely, ZnO:Zn, existed, for use in low voltage field emission devices. In our proposal we outlined some lattices which we intended to develop for achieving a full colour gamut display, together with a novel approach for achieving 'intrinsic' surface conductivity felt necessary for FEDs. Some of these lattices were gallates, borates and stannates. The ZnO:Zn phosphor was to be developed so that a performance equalling or exceeding that of commercially available phosphor was realised.

In addition, techniques were to be developed permitting fabrication of very small particle sized conducting powders, such as In_2O_3, ITO and SnO_2, for phosphors where sufficient conductivity was not achieved in the time available. Furthermore, where possible, thin film phosphors were to be attempted so that very high resolution FEDs could be realised.

Finally, a new low voltage demountable CRT system, similar to the one available at Fort Monouth, was to be assembled, permitting useful exchange and verification of results.

Over the last year, considerable progress has been made. Of particular interest has been the development of a saturated green emitting phosphor ($ZnGa_2O_4$:Mn) and an orange-red emitting phosphor ($CaTiO_3$:Pr). Both these phosphors are excitable below 500V. Luminance levels achieved so far with early samples have been 350 ft-L ($ZnGa_2O_4$:Mn) and 160 ft-L ($CaTiO_3$:Pr). The results obtained from in-house prepared ZnO:Zn phosphor have also been encouraging yielding 2600 ft-L (cf. commercial phosphor ~2700 ft-L). Hence, in our first year, we have made available a green, an orange-red and a blue-green phosphor system capable of being excited at low voltages for use in FEDs.

Experiments engineered to provide surface conduction to normally insulating phosphor have also been successful and conductive $InBO_3$:Tb phosphor has been made. Very fine particle ITCO powder (<1000A) has been prepared with high conductivity. Photoluminescent thin films of ZnO:Zn and $ZnGa_2O_4$:Mn have been made by a novel aerosol spray pyrolysis method.

As far as we know, this is the first time that PL thin films of $ZnGa_2O_4$:Mn have been made. The emission colour under UV excitation appears identical for both powder and thin films

gallates, as were the XRD spectra. Samples of ZnO:Zn and $ZnGa_2O_4$:Mn thin films have been forwarded to ETDL.

Early stability measurements under CR excitation have been performed on ZnO:Zn, $ZnGa_2O_4$:Mn, $CaTiO_3$:Pr and $InBO_3$:Tb phosphors. Apart from ZnO:Zn, the phosphors appeared fairly stable with $ZnGa_2O_4$:Mn showing the best stability.

More recently, SnO_2:Eu and Zn_2SnO_4:Eu phosphors have been made. The PL from SnO_2:Eu appears orange-red but the emission from Zn_2SnO4:Eu is weak.

Hence, a whole range of phosphors, both in powder and thin film form, are being developed. Our future plans are outlined in the next section.

15) Future Work

As noted above, so far, the work has been on target and, in fact, exceeded our expectations, resulting in a three-colour phosphor system, compared to only one colour a year ago. However, for a fully saturated RGB system, any FED prepared at this time would require colour filters, especially for the blue from ZnO:Zn. In addition, there are other aspects of phosphors which must be matched in a true RGB system. These include phosphor rise and decay times (persistence), temperature stability, degradation rates, B-V performance, particle size, deposition techniques and so on. We should also aim to make phosphors with lower threshold voltages so that future FEDs are compatible with TFT drive.

Hence, apart from improving the phosphors which we have made, we need to tackle the above mentioned issues. We would prefer to engineer stand-alone phosphors, i.e. those not requiring filters. Efforts are already in hand to alter persistence characteristics of the $ZnGa_2O_4$:Mn and $CaTiO_3$:Pr phosphors with some success achieved already. Although early samples of ZnO:Zn and $ZnGa_2O_4$:Mn thin film phosphors appear promising, other thin film lattices are being investigated.

Briefly, our programme for the remaining year can be summarised as noted below:

1) Evaluation of all samples using the low voltage cathodoluminescent system.

2) Preparation of improved thin films of ZnO and $ZnGa_2O_4$:Mn.

3) Preparation of SnO_2:Eu and/or $CaTiO_3$:Pr thin films.

4) Set up assembly system for small, sealed devices.

5) Initiate further collaboration with FED consortia.

6) Continue supply of samples to ETDL and reports to ETDL and ERO.

XRD spectrum of: Fig. 1) zinc oxide, raw material;
Fig. 2) zinc oxide phosphor; Fig. 3) zinc oxide
phosphor with added sulphur.

Fig. 1

Fig. 2
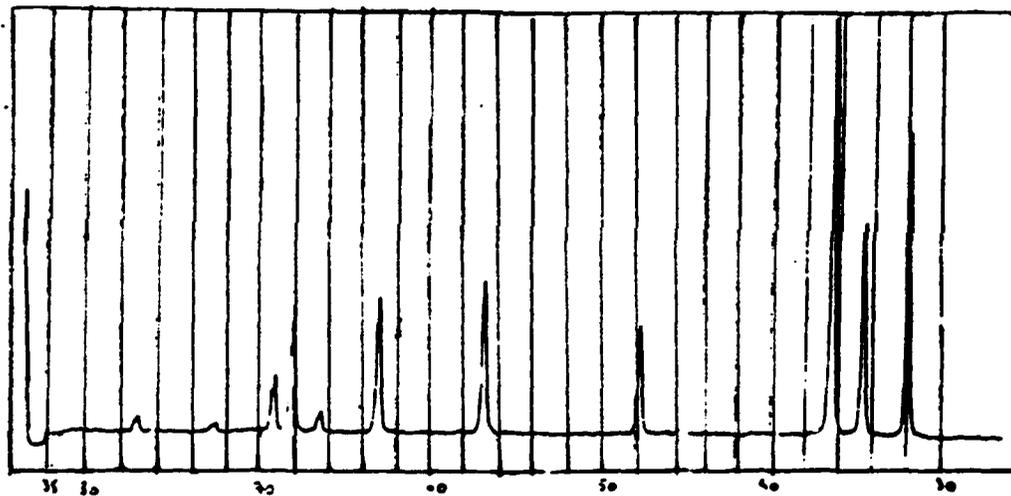
Fig. 3

Fig. 4   SEM micrograph of commercial ZnO:Zn phosphor
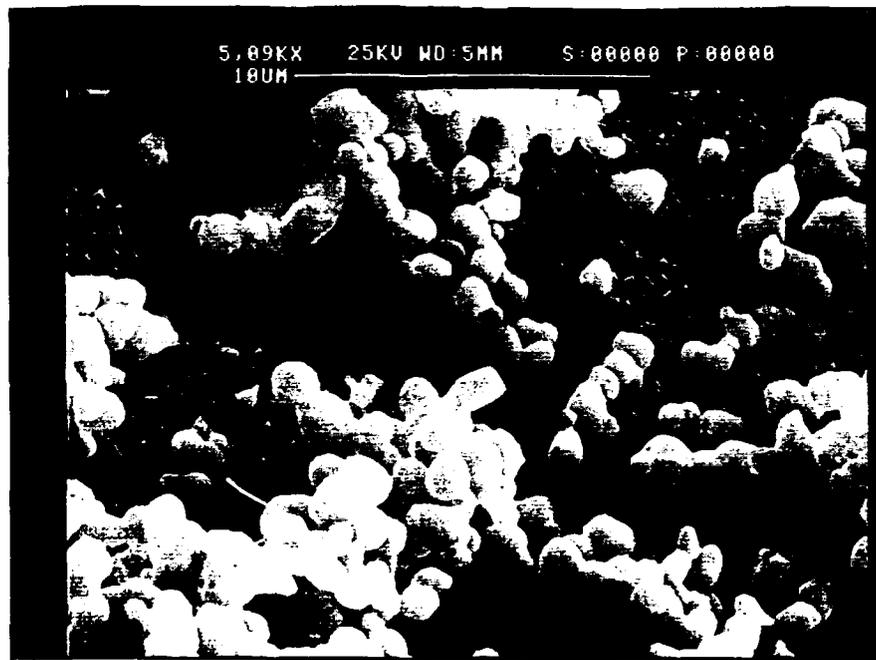
Fig. 5   SEM micrograph of in-house ZnO:Zn phosphor
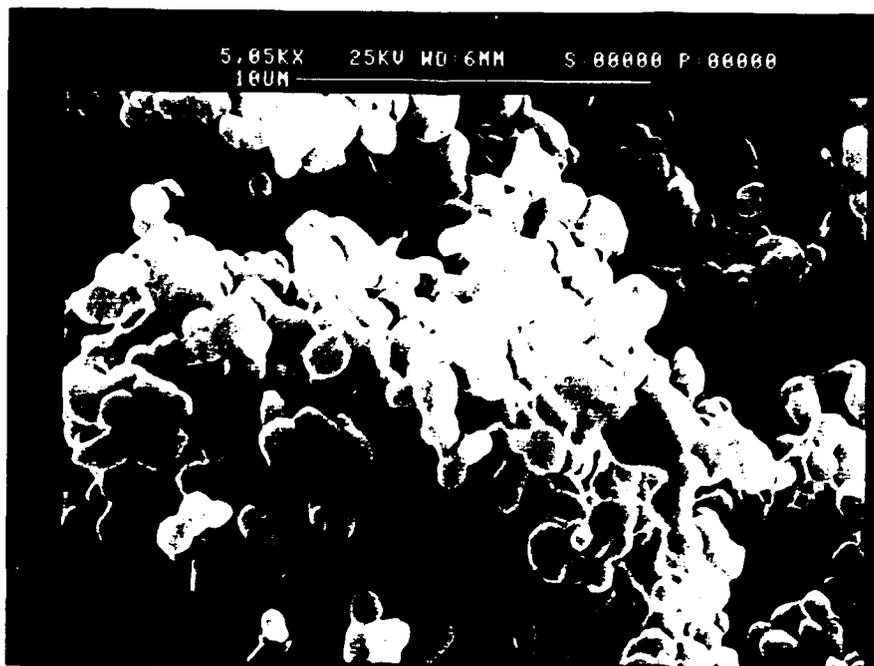
Fig. 6   Dissociation plot for Zn-O

$p_{Zn} \cdot p_{O_2}^{\frac{1}{2}} = 10^{-6}$ atm$^{\frac{3}{2}}$

$P_{tot} = p_{Zn} + p_{O_2}$

P_{tot}

minimum vapor pressure
$p_{Zn} = 2 p_{O_2}$

p_{Zn}

p_{O_2}

p (atm)

p_{Zn} (atm)

$4 \cdot 10^{-5}$ $8 \cdot 10^{-5}$ $1.2 \cdot 10^{-4}$ $1.6 \cdot 10^{-4}$ $2.0 \cdot 10^{-4}$ $2.4 \cdot 10^{-4}$

$4.0 \cdot 10^{-4}$
$3.6 \cdot 10^{-4}$
$3.2 \cdot 10^{-4}$
$2.8 \cdot 10^{-4}$
$2.4 \cdot 10^{-4}$
$2.0 \cdot 10^{-4}$
$1.6 \cdot 10^{-4}$
$1.2 \cdot 10^{-4}$
$8 \cdot 10^{-5}$
$4 \cdot 10^{-5}$
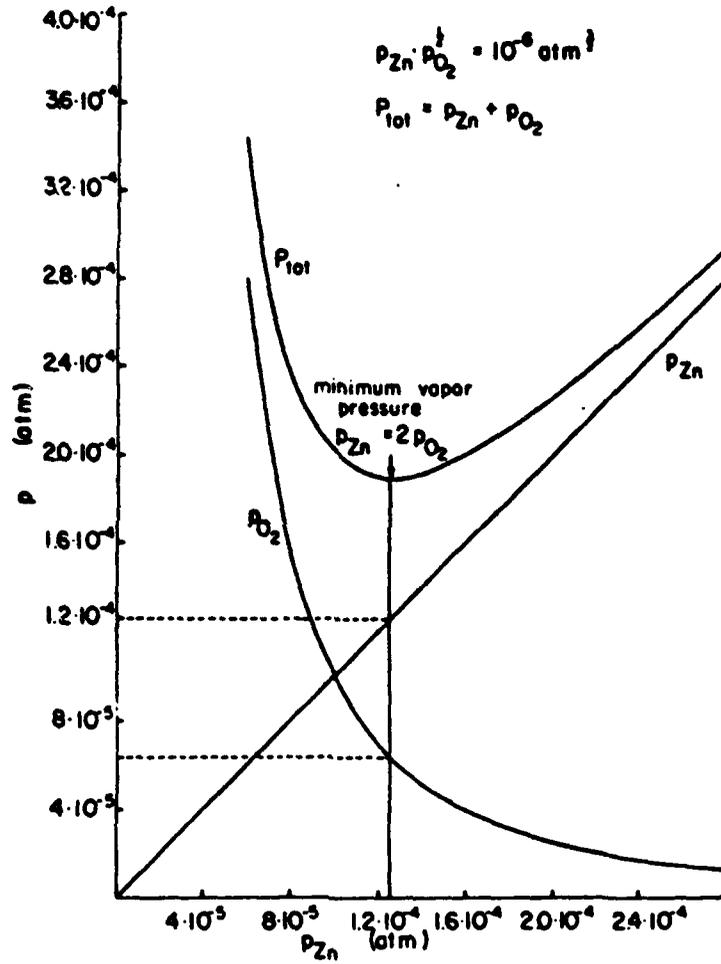
Fig. 7   Excitation and emission spectra of ZnO:Zn
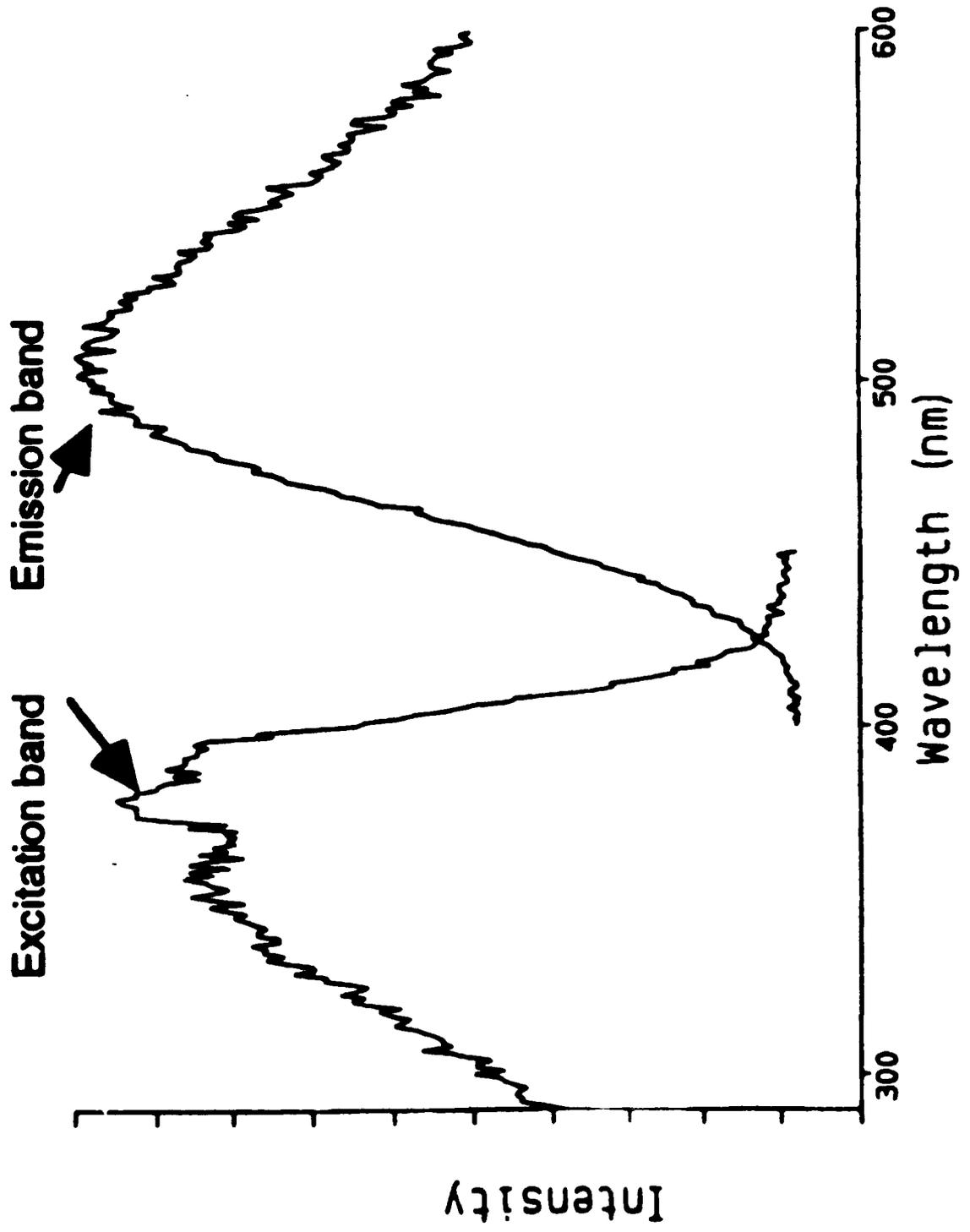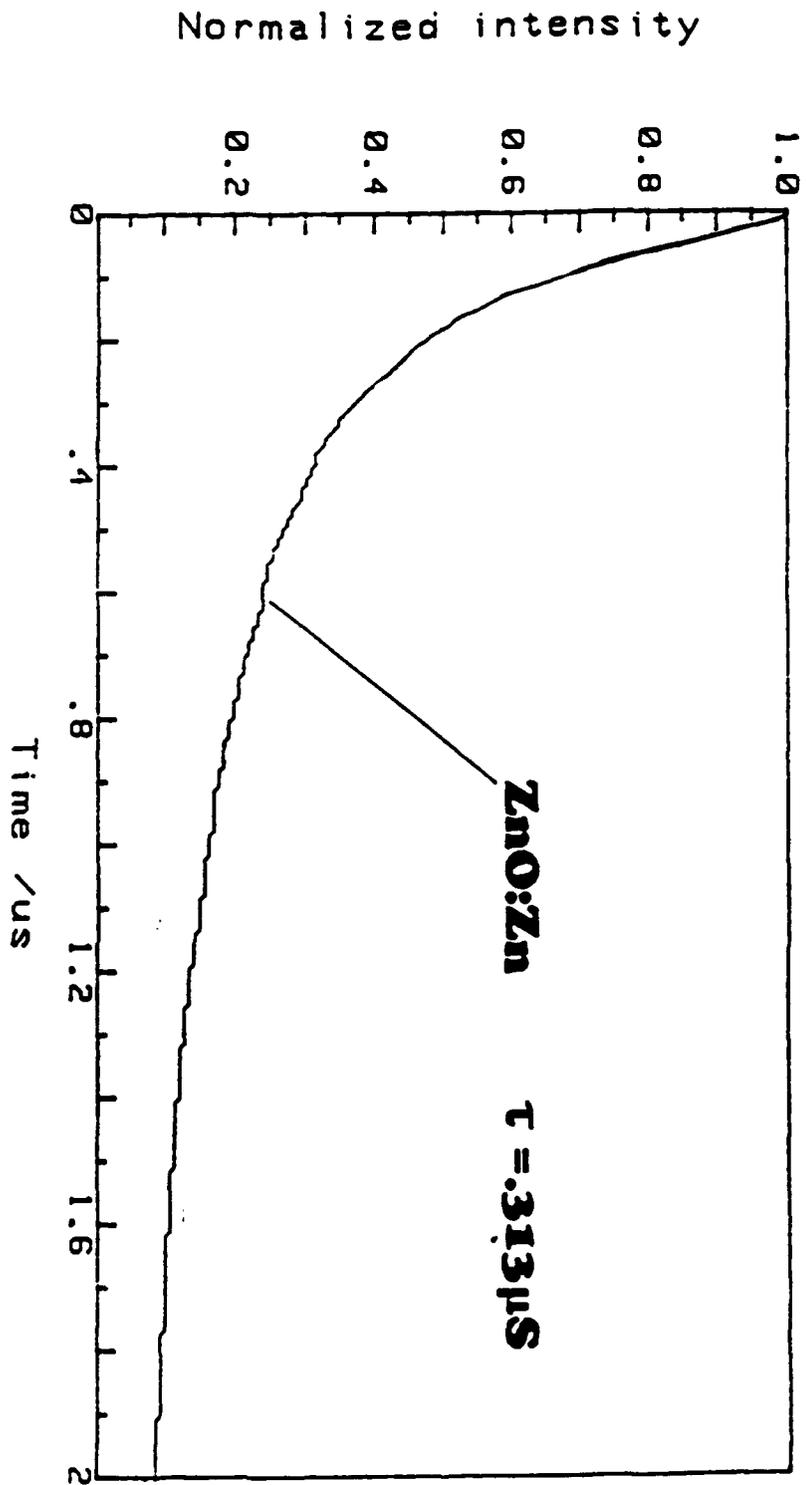
Fig. 8 **PL decay profile of ZnO:Zn**

ZnO:Zn $\tau = .313 \mu S$
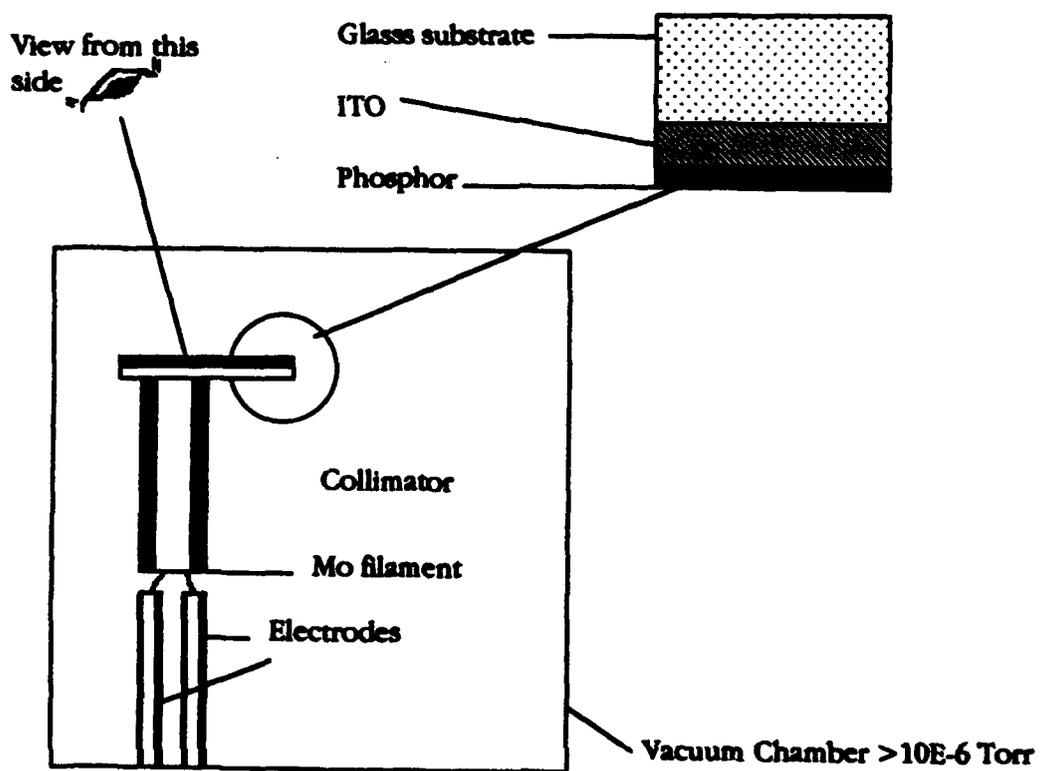
1. Heat Mo Filament
2. Apply EHT between the ITO and the base plate of the vacuum chamber

Fig. 10   Brightness voltage curve for zinc oxide zinc
          phosphors, (LEP31, 32, University of Greenwich;
          LEP33, commercial phosphor).
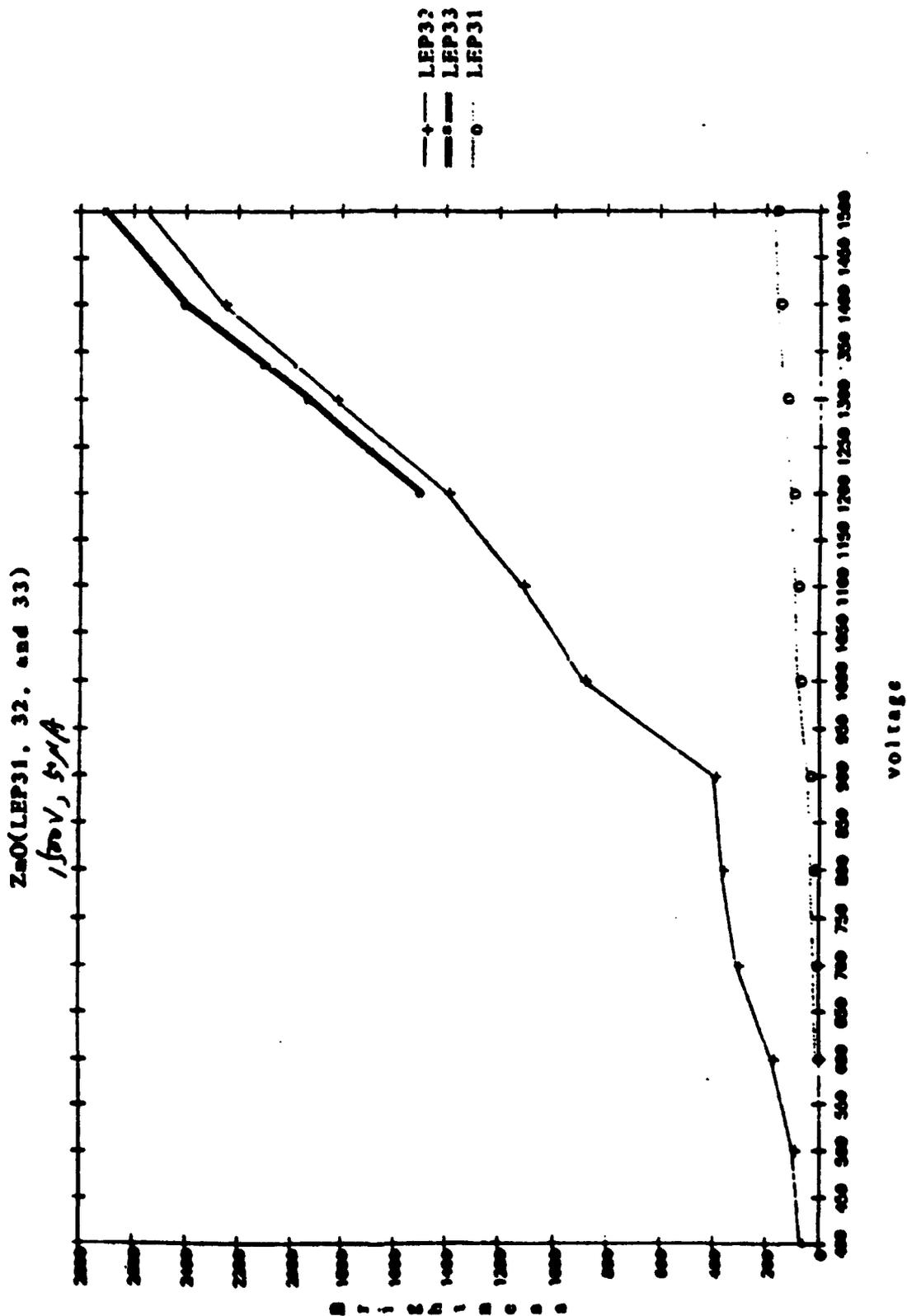
Fig. 11 **Maintence Curve for LEP32 (5um) ZnO:Zn at 1500 U and 10 uA**
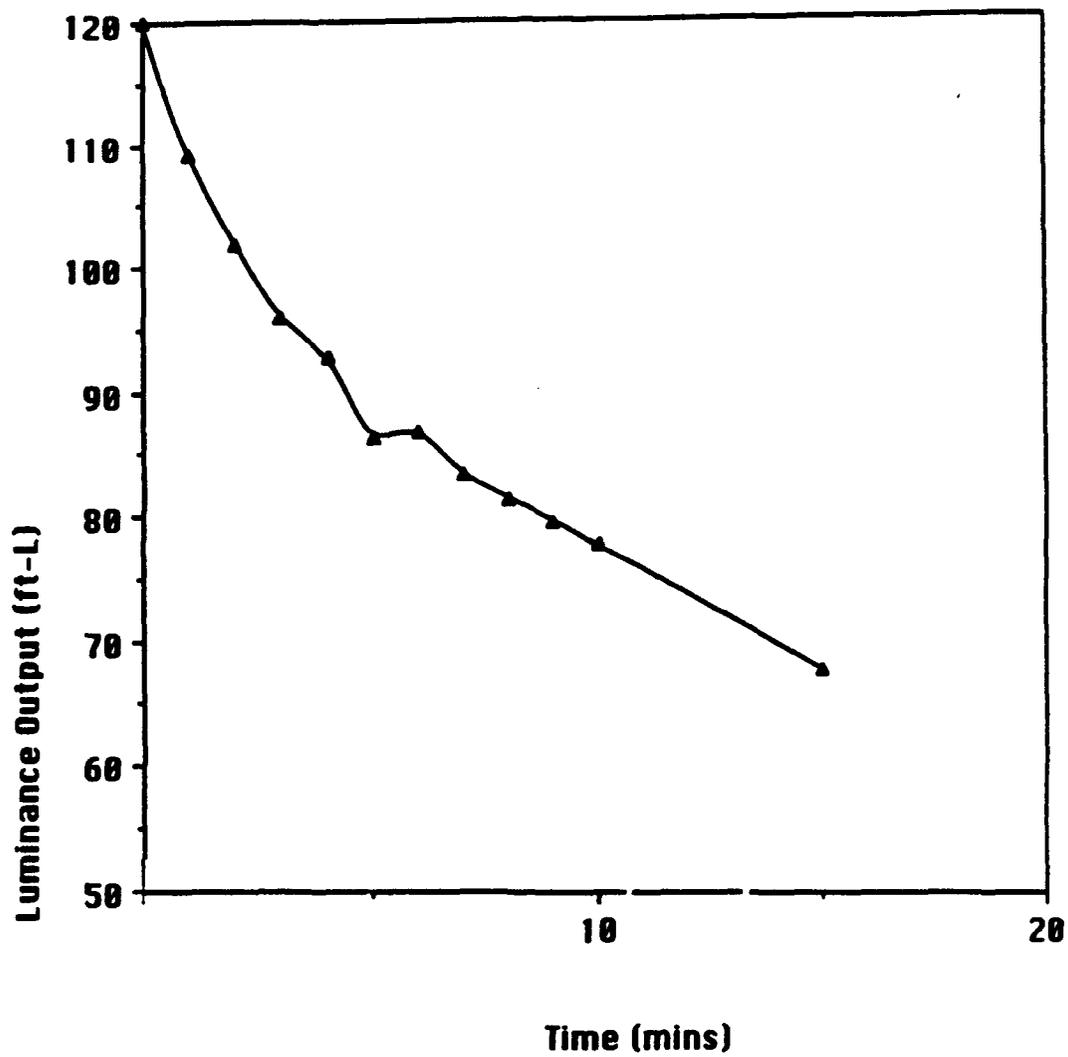
Fig. 12   SEM micrograph of $ZnGa_2O_4$:Mn

Fig. 13   Excitation/emission of $ZnGa_2O_4$:Mn

Fig. 13   Excitation/emission of $ZnGa_2O_4$:Mn

Normalized intensity

GaII:Mn   τ=4.188 mS

Time /ms
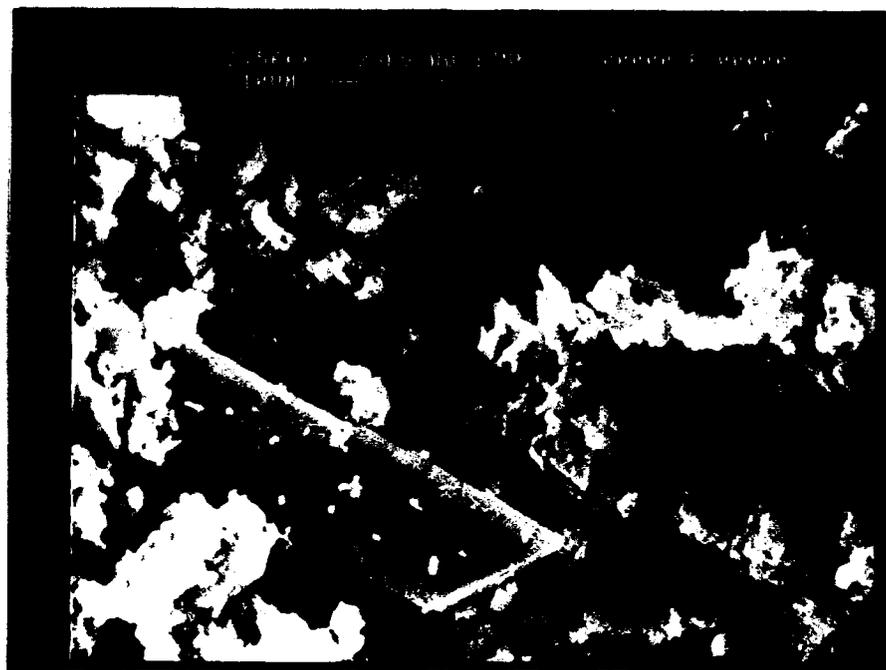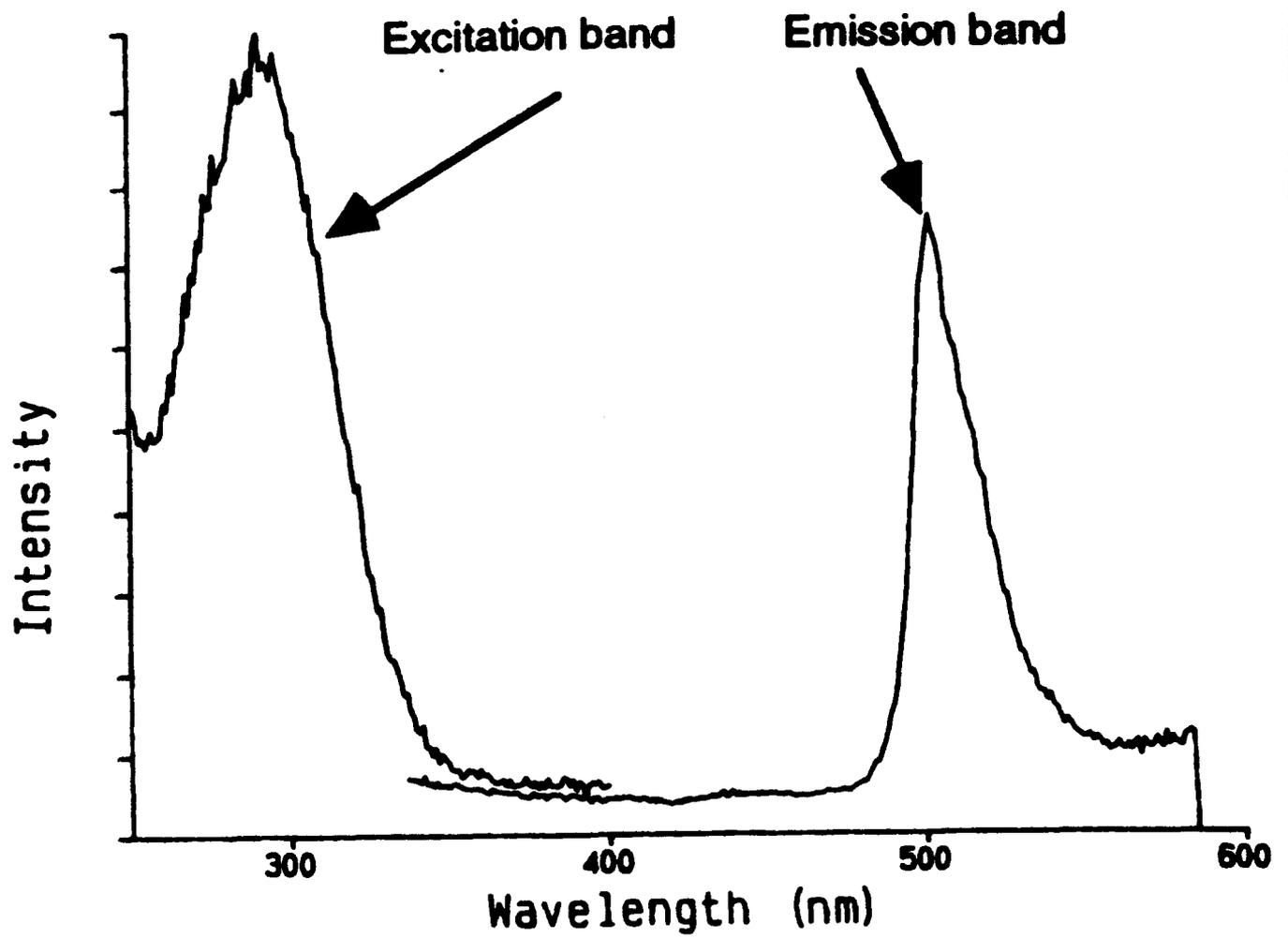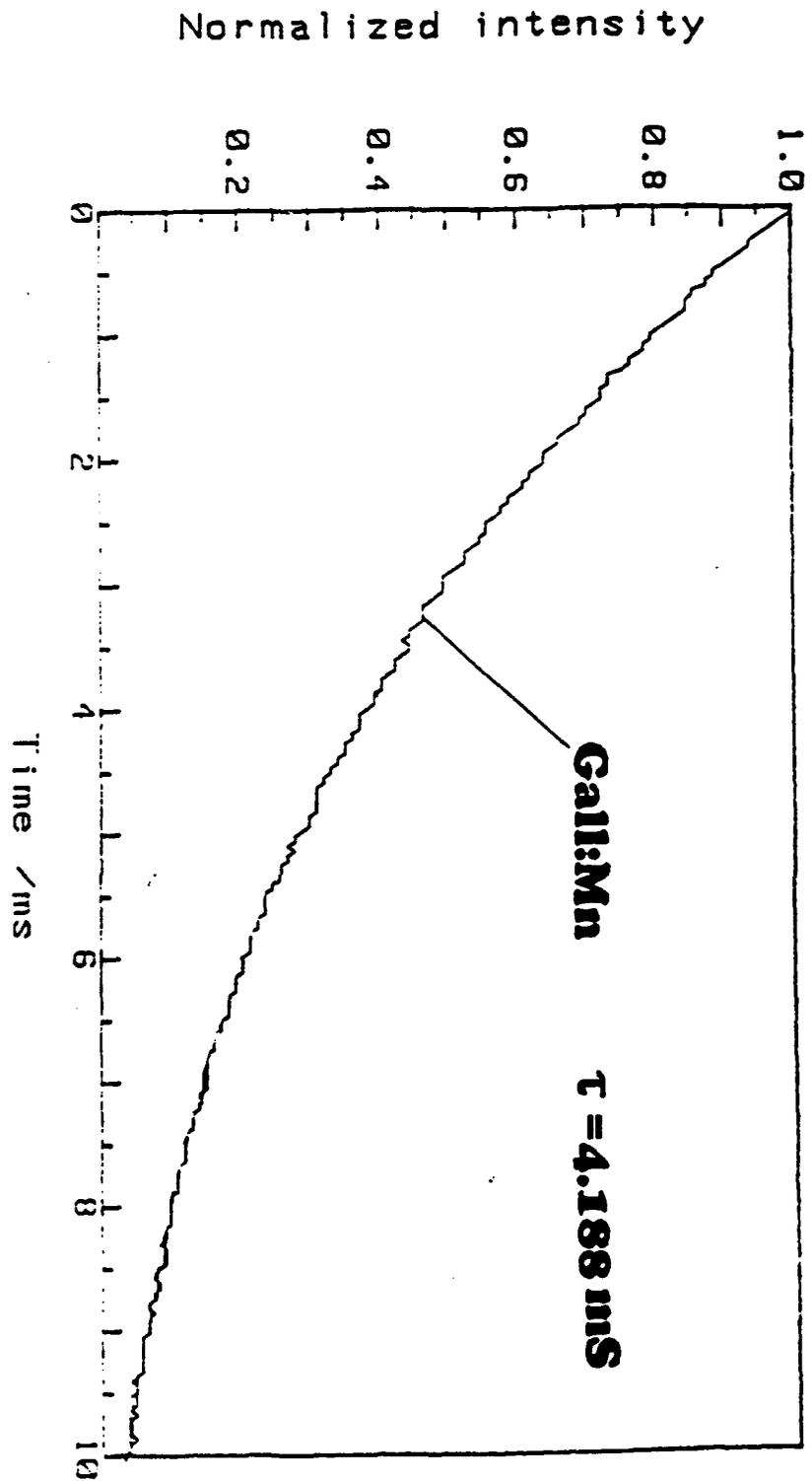
Fig. 14   PL decay profile of GaII:Mn

Fig. 15 CL spectrum of gallate phosphor

Intensity (cps)

2.751e+06

—— LEP6_01.CRT 1Kev/30uAemission/1.1v/1.6a
—— LEP6_02.CRT 500ev/30uAemission/1.1v/1.6a

Wavelength (nm)
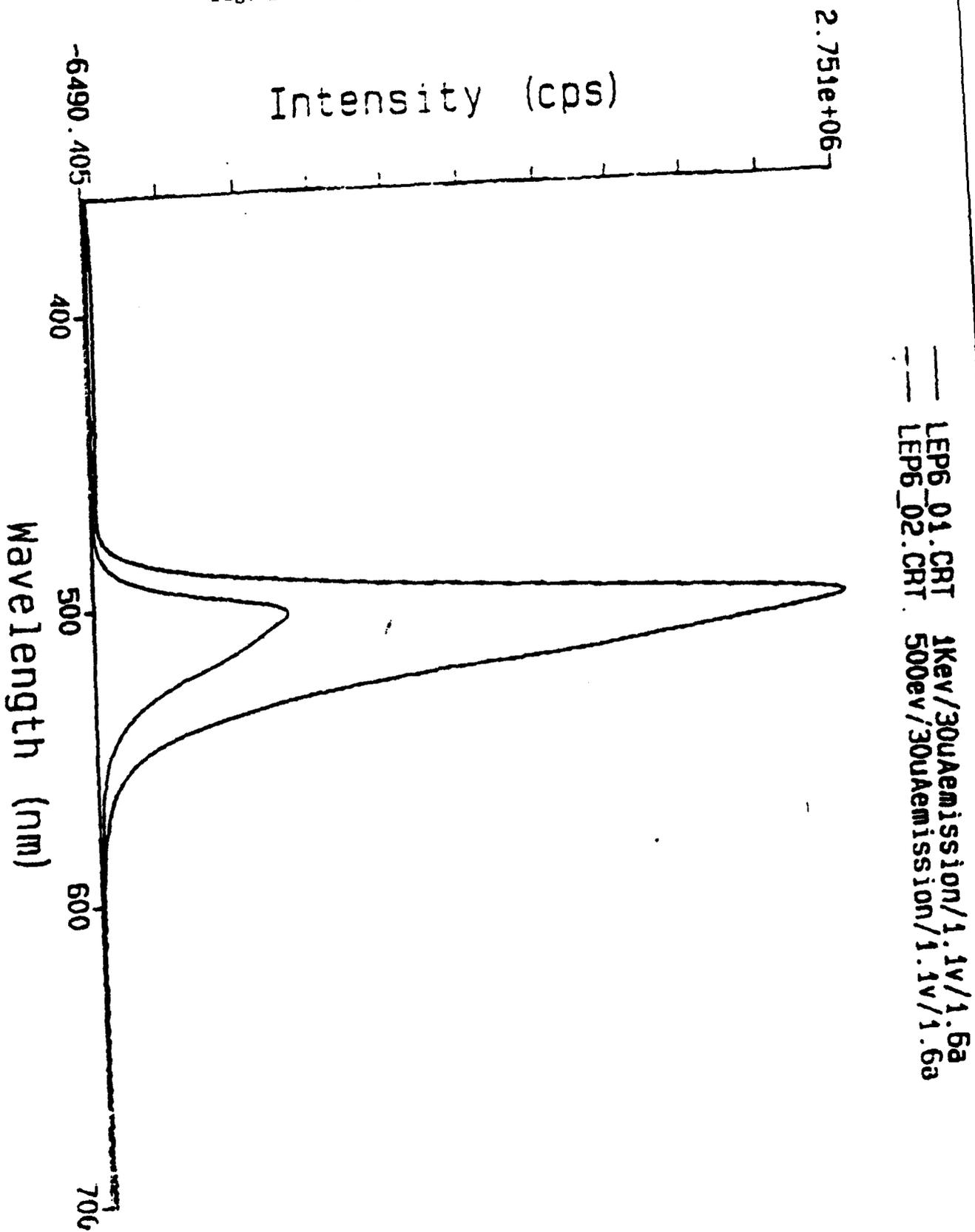
Fig. 16 Luminance Output (ft-L) as a Function of the Applied Voltage (V)
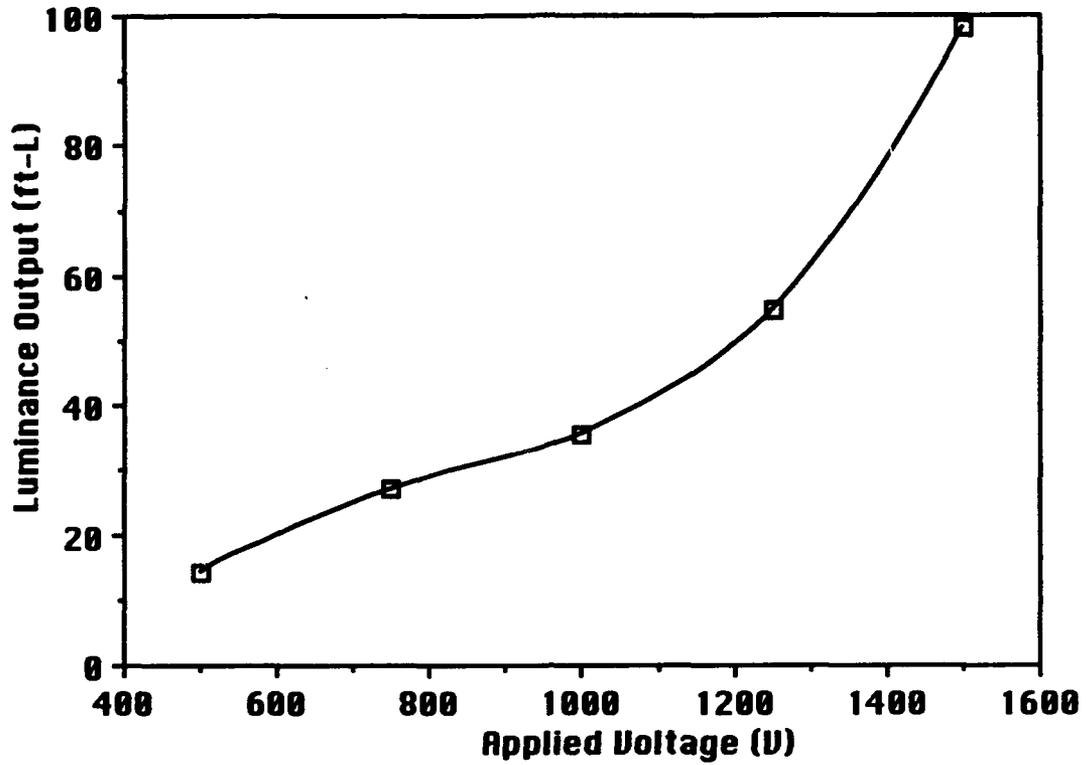
Fig. 17 Maintenance Curve for LEP38 (ZnGA2O4:Mn) at 1500 V and 10 uA

Luminance (ft-L)

15 um layer with 46% transmission

Current (uA)

(a)

(b)
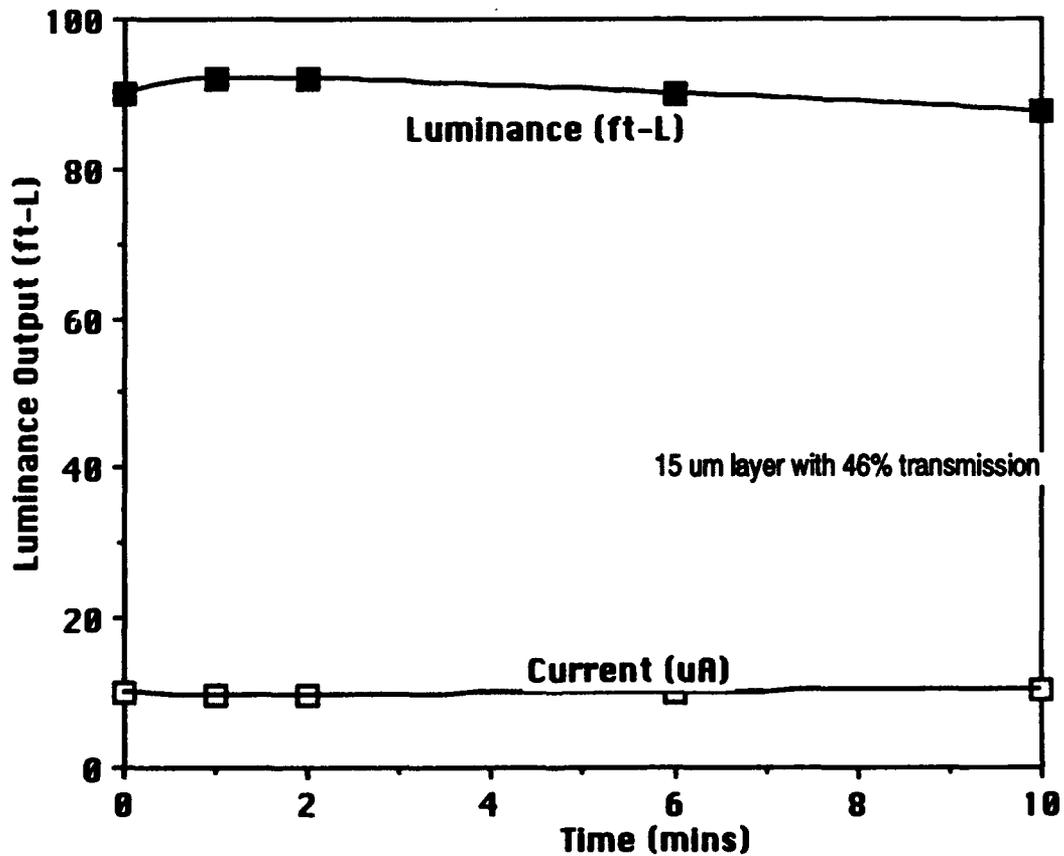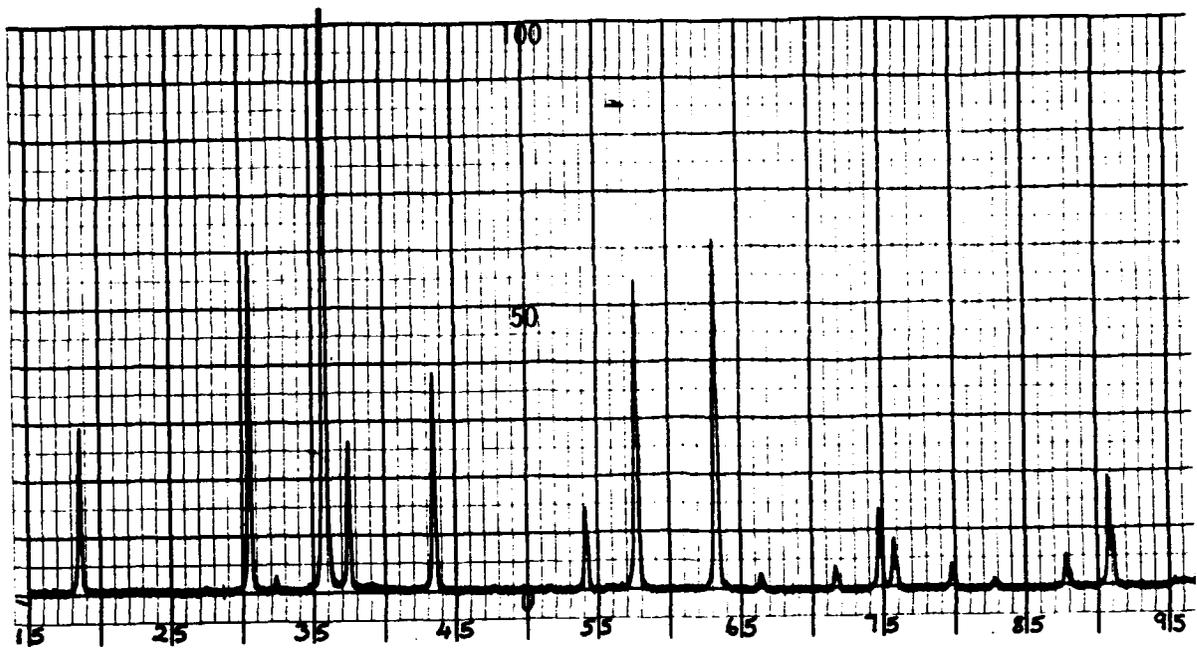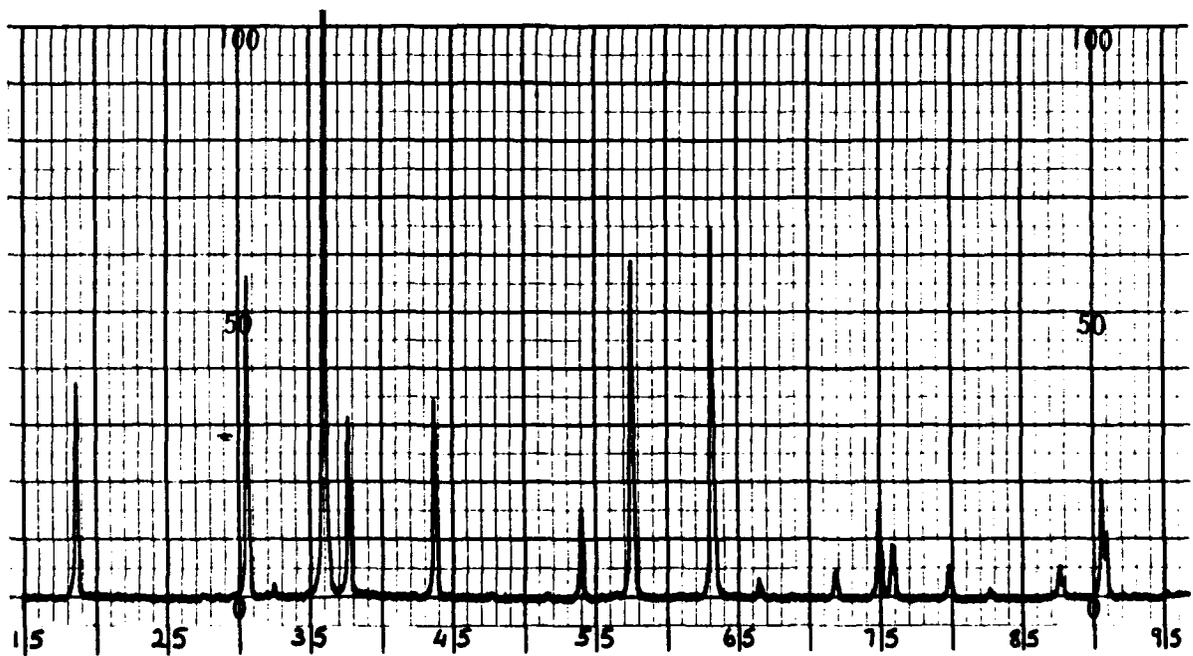
XKD of gallate phosphor showing Fig. 18) long persistence (a),
and Fig. 19) short persistence (b).

Fig. 20   XRD plot of titanate phosphor
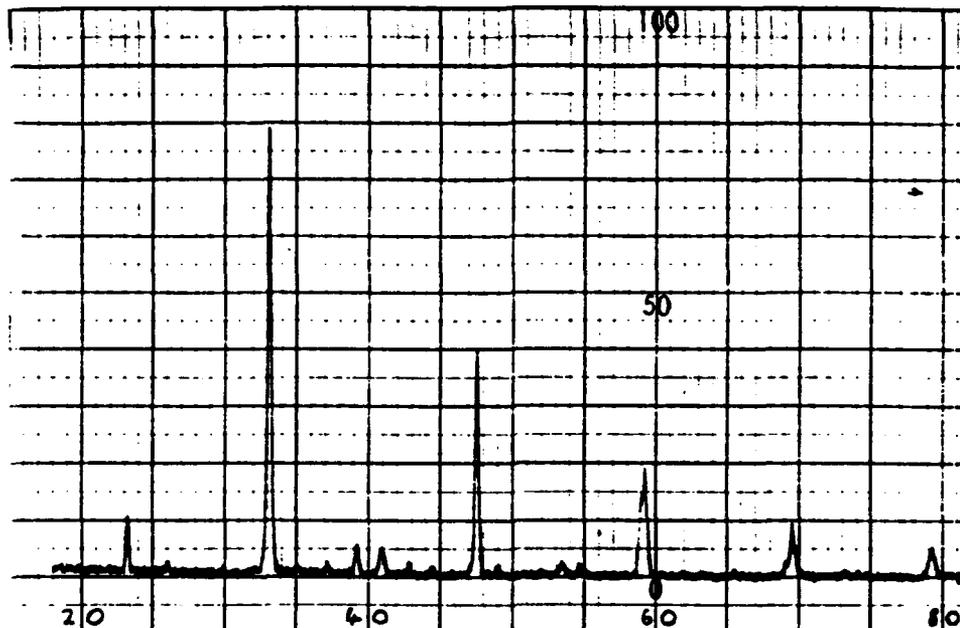
Fig. 21   SEM micrograph of titanate phosphor
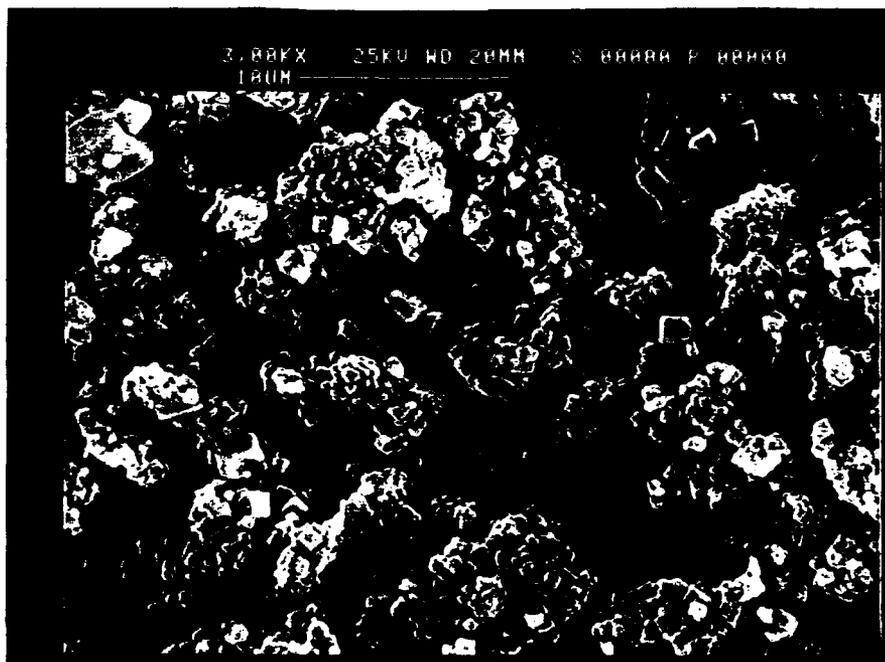
Fig. 23 EMISSION SPECTRA OF CALCIUM TITANATE:Pr PHOSPHOR UNDER LOW VOLTAGE CATHODE RAY EXCITATION
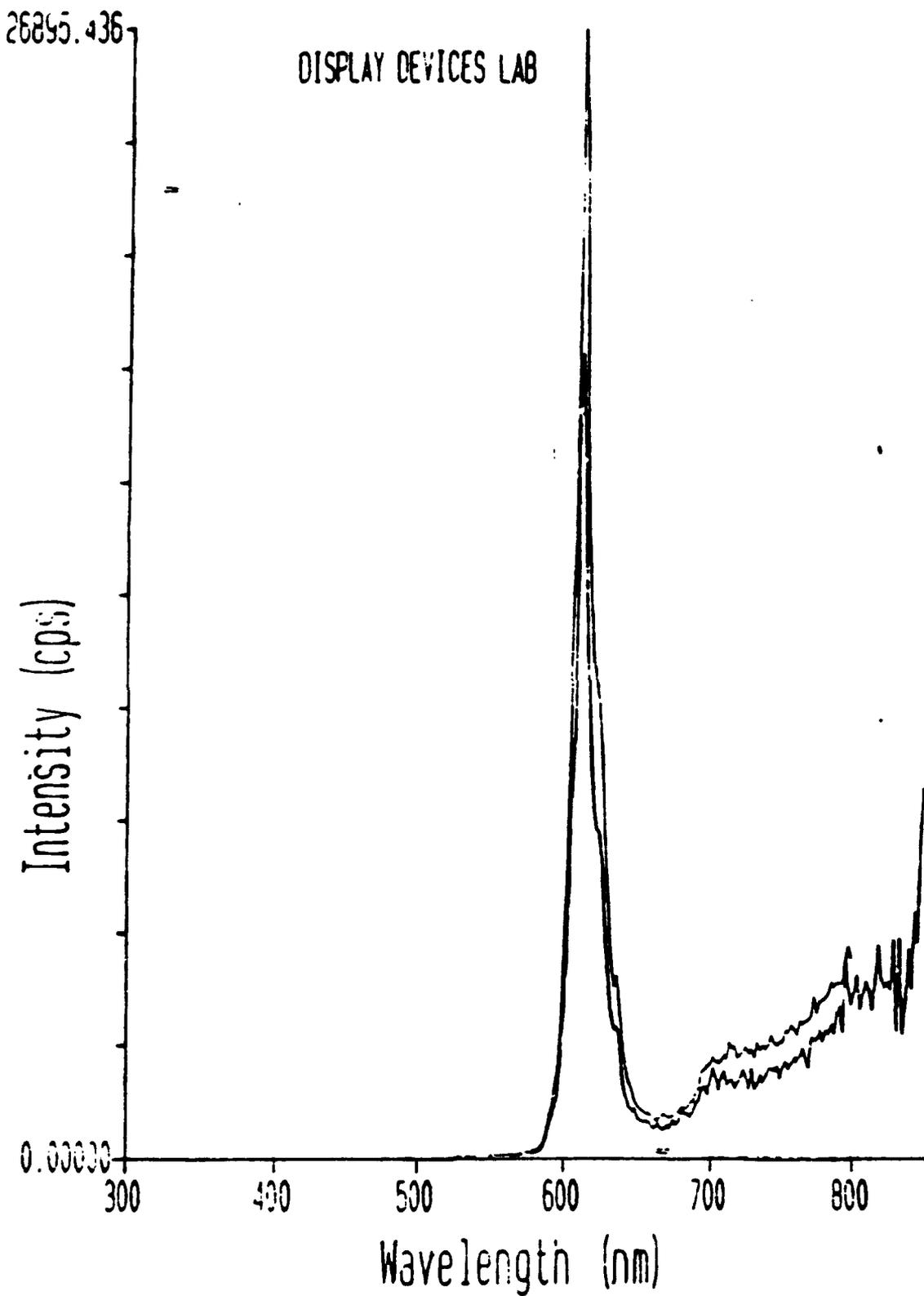
Fig. 24   Brightness voltage curve of the red emitting calcium
strontium titanate phosphor at high loading

RED (LEP34, 35, 36, and 37)
(μW, PM)

LEP34 (1Ca:08Sr)
LEP37 (1Ca:08Sr)
LEP35 (3Ca:1Sr)
LEP36 (1Ca:1Sr)
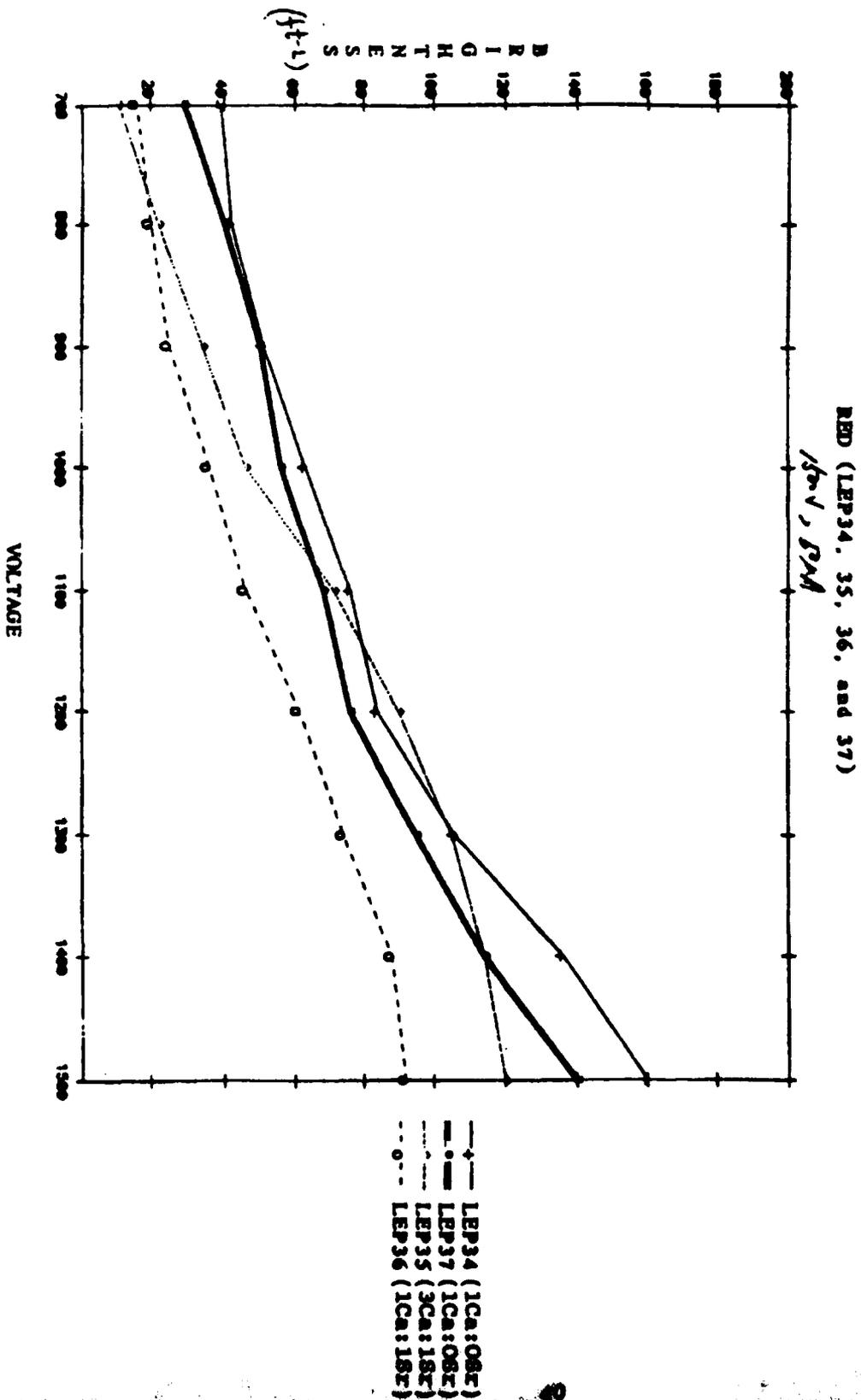
Fig. 28 Brightness voltage curve of $CaTiO_3:Pr$ at low loading

LEP37_CR   CR measurement   05-JAN-93 10:16 Page 1
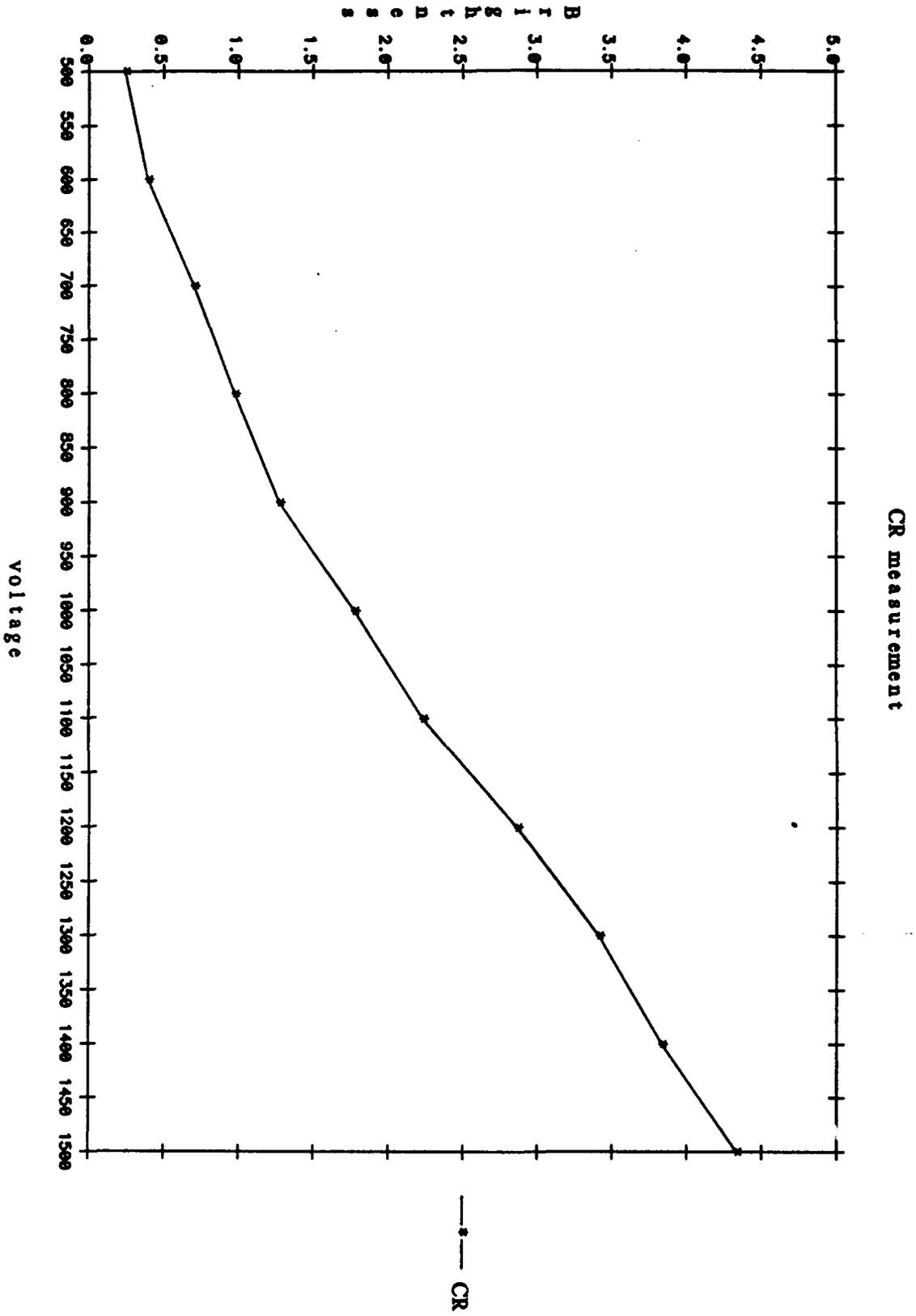
Fig. 26   Maintenance Curve for CaTiO3:Pr Phosphor at 1500 U
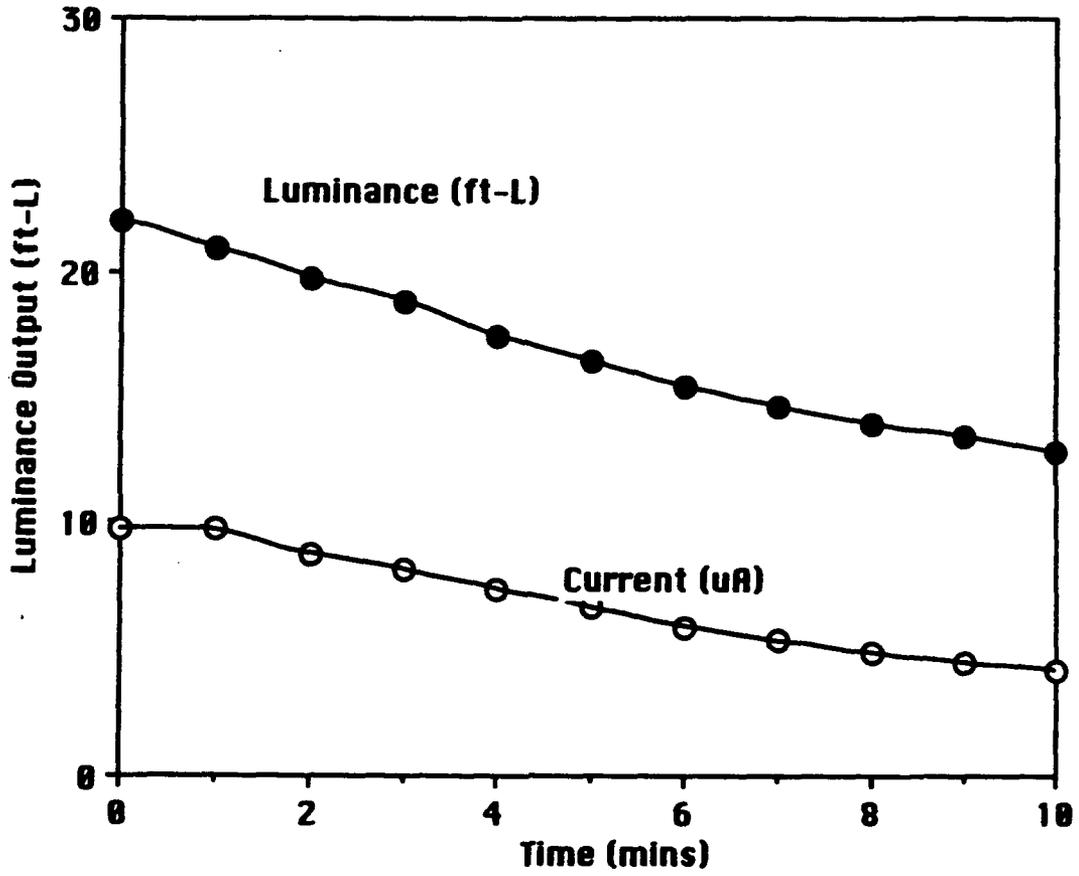
Fig. 27   SEM micrograph of SnO_2:Eu
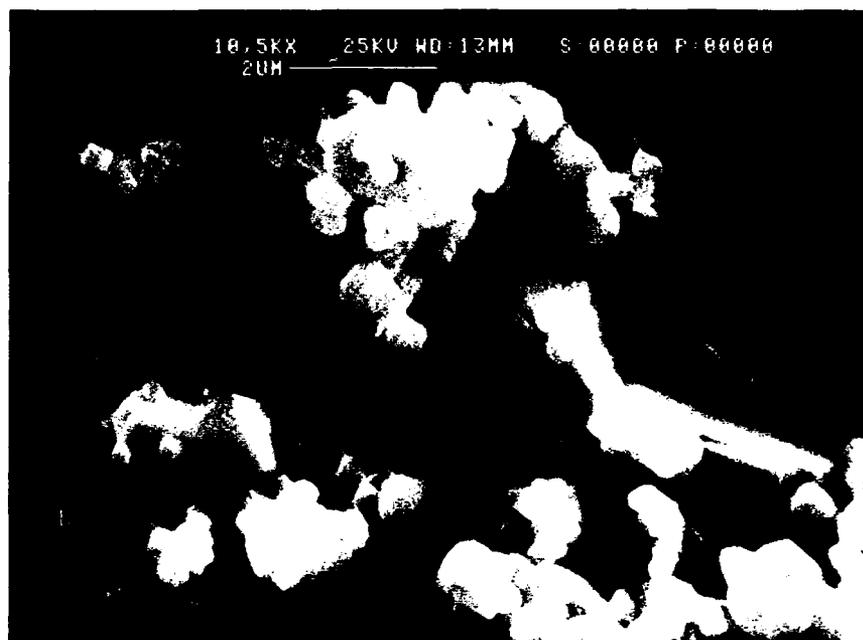
Fig. 28   XRD of SnO_2:Eu
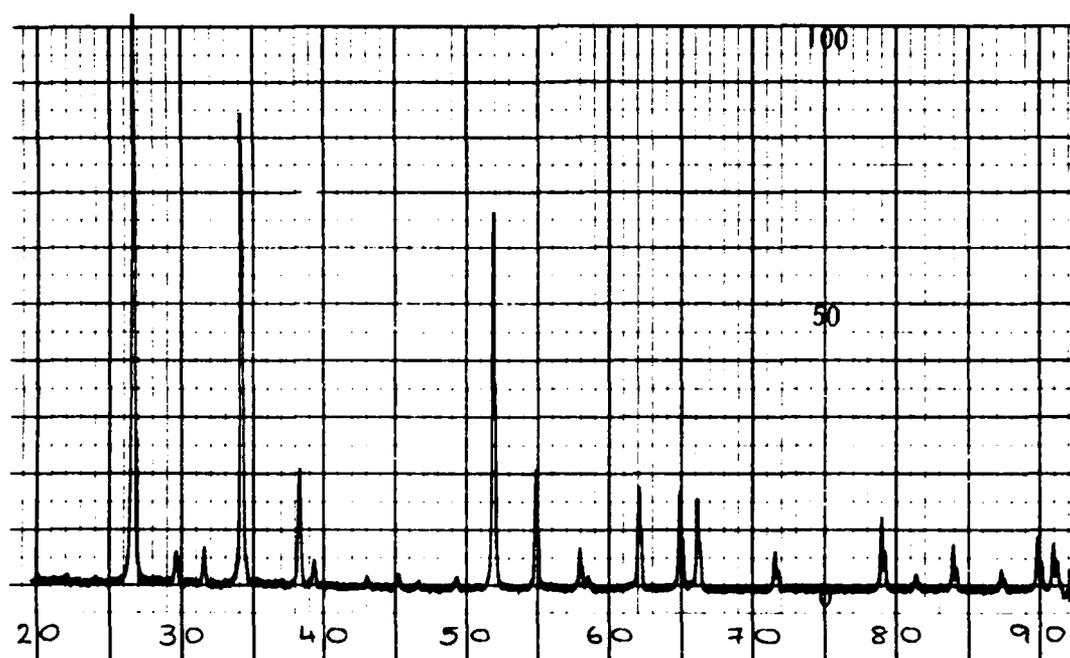
Fig. 29   SEM micrograph of Zn_2SnO_4
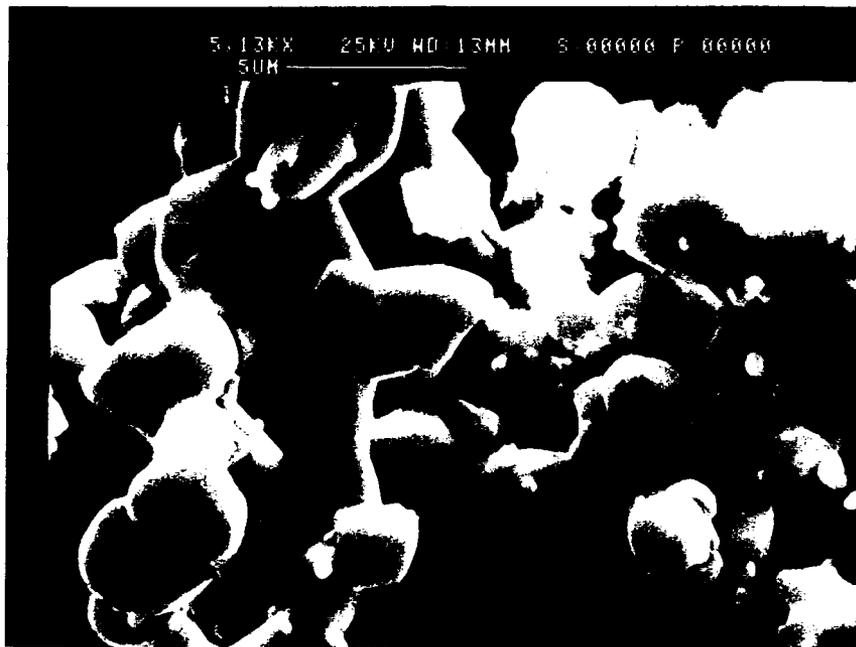
Fig. 30   XRD of Zn_2SnO_4
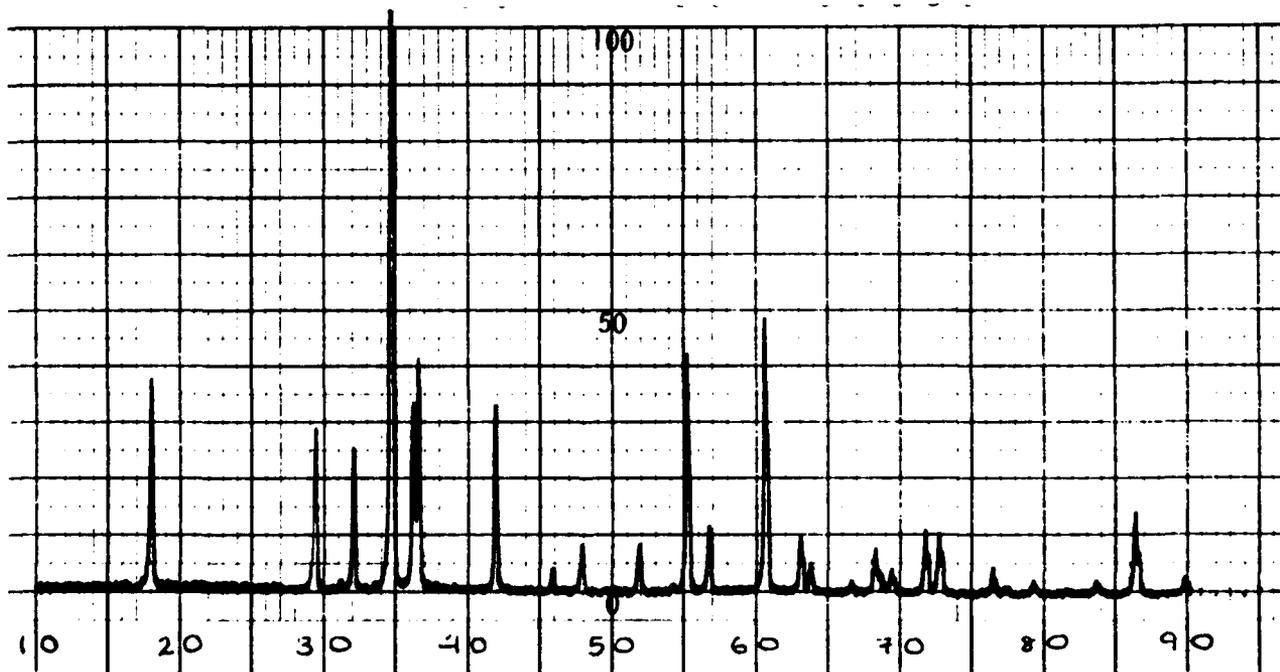
Fig. 31   Simplified sketch of apparatus used for ASP.

PRECURSOR SOLUTION
RESERUOIR
(500 ml dropping funnel)

PVC
CONNECTION
TUBE

TO GAS CYLINDER
UIA FLOWMETER
(DILUENT GAS)

NEBULISER
(CORNING FLAME
PHOTOMETER
ATOMISER)

SS TUBING
CONTAINING THERMOCOUPLE
SERUING AS HANDLE FOR
SUBSTRATE PLATFORM (NOT SHOWN)

GAS DELIUERY
TUBE

REACTION CHAMBER
(AI ALLOY)
SEATED ON
HOTPLATE

MIST CHAMBER
(2 L 3 NECKED
OF FLASK)

TO WASTE
RESERUOIR

TO DIGITAL
THERMOCOUPLE

Fig. 32a   Sketch of reaction chamber.

SUBSTRATE PLATFORM
INSERTED HERE THROUGH
OPEN END

ENTRY PORT
FOR MIST
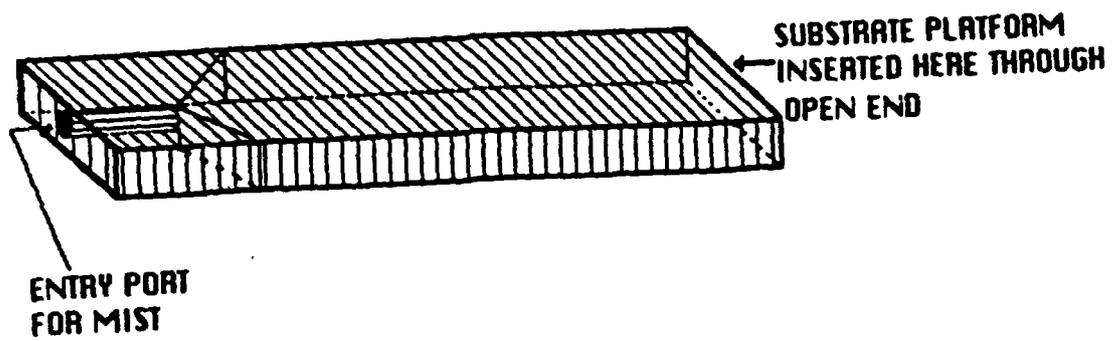
Fig. 32b   Sketch of substrate platform.

STAINLESS STEEL TUBE
TO CENTRE OF
PLATFORM SERVING
AS HANDLE AND
ACCOMMODATING
THERMOCOUPLE
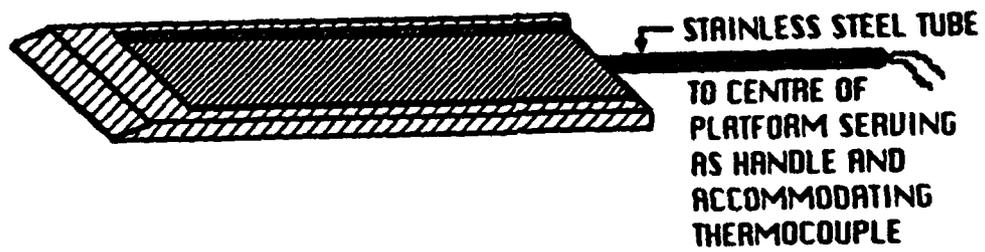
Fig. 33   UV/Vis spectrum of a zinc oxide film on
sapphire (used for determining the thickness
of the zinc oxide thin films).

47
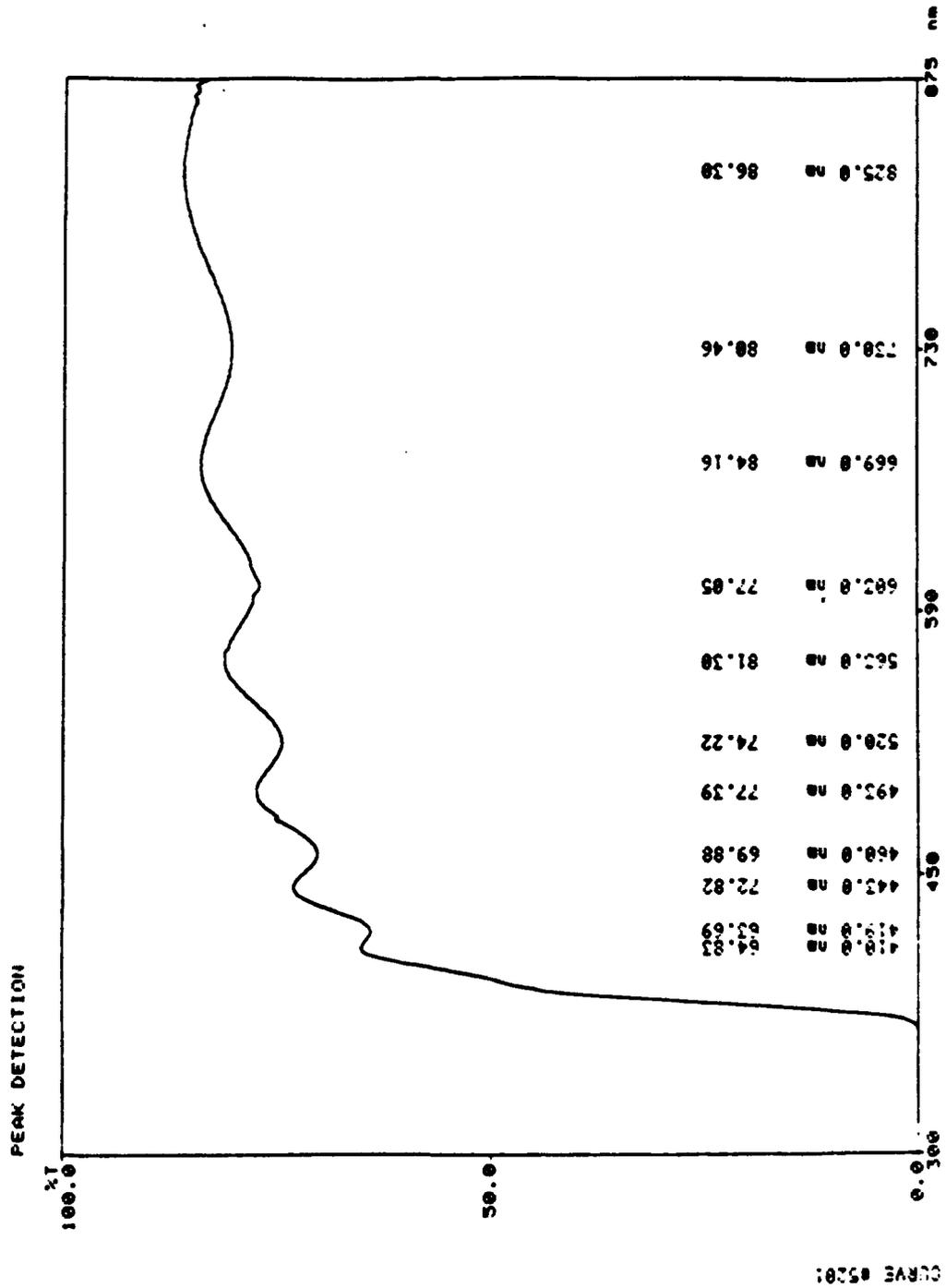
Fig. 34   SEM micrograph of unannealed ZnO on Glass
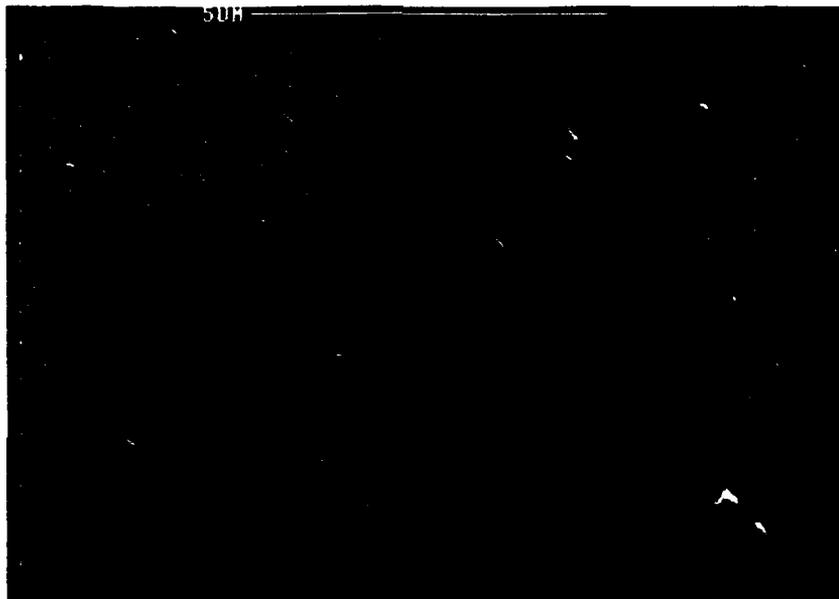
Fig. 35   UV/VIS spectrum of zinc gallate thin film
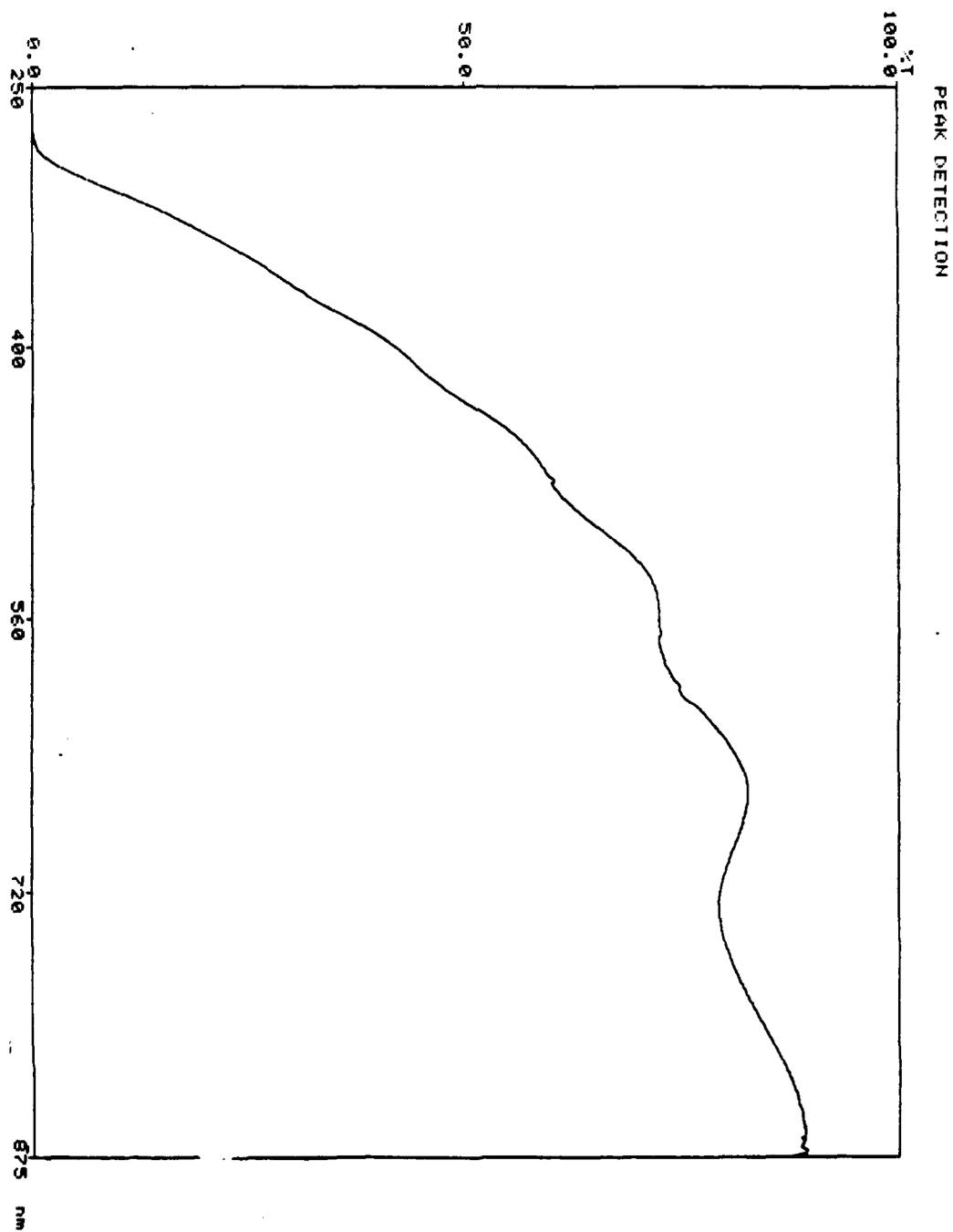
Fig. 36   XRD of ZnGa$_2$O$_4$:Mn thin film
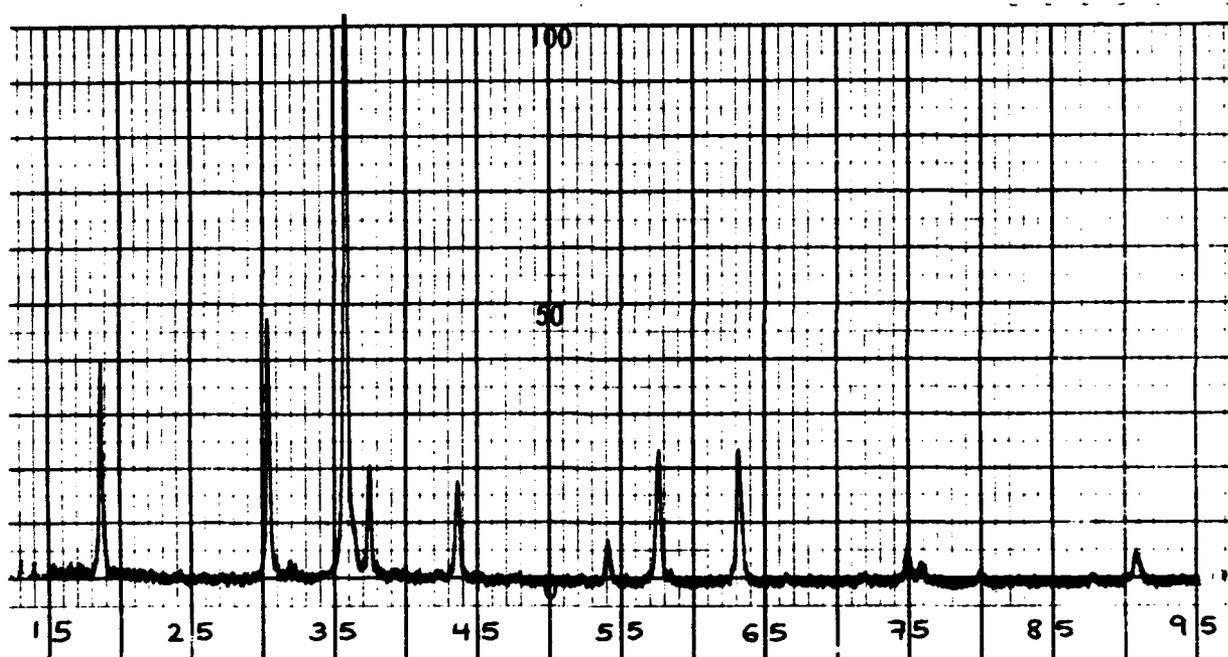
Fig. 37   Tin concentration in ITCO powder
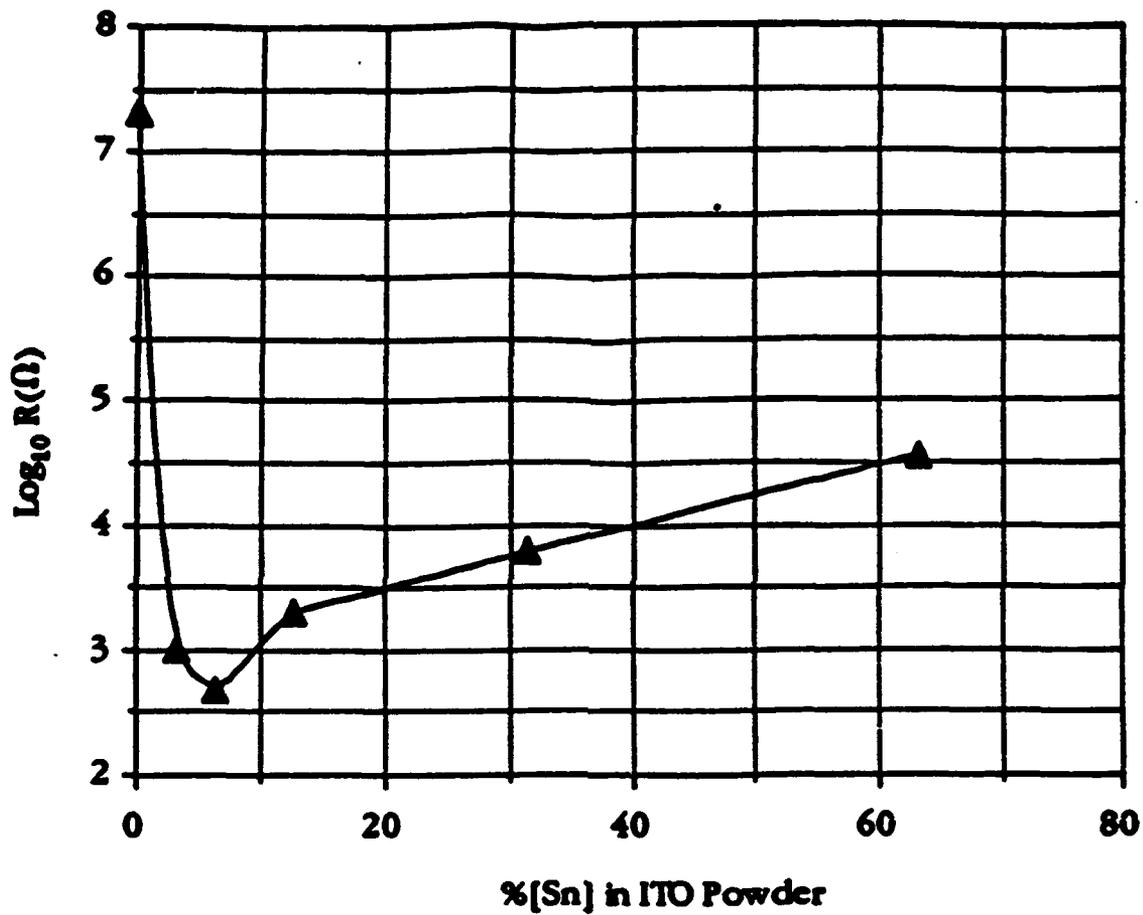
Fig. 38   Low voltage demountable cathode ray apparatus
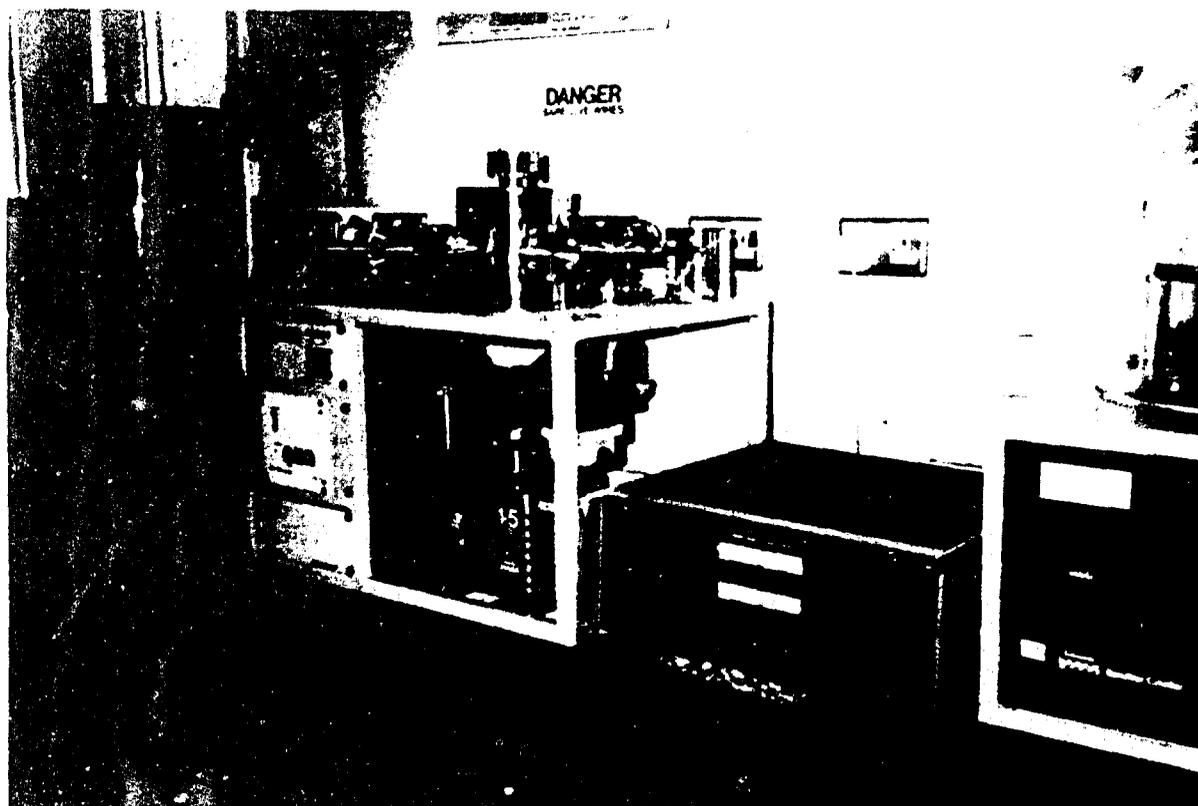
Fig. 39   Close-up of electron gun